Measurements of Microwave Spectra and Structural Parameters for Cyclopentadienylchromium Dicarbonyl Nitrosyl

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Microwave rotational spectra were measured for eight isotopomers of η^5-$C_5H_5Cr(CO)_2NO$ using a pulsed-beam, Fourier transform spectrometer. The normal isotopomer is a near-symmetric rotor with $A = 1001.693(2)$, $B = 797.2724(6)$, and $C = 797.0143(6)$ MHz. This complex has a "piano-stool" type structure, with one symmetry plane. The accidental, near-symmetric top inertia tensor gives a clear indication of different bonding and structural parameters for the nitrosyl group and the carbonyl groups, since 3-fold symmetry for the nitrosyl and carbonyl groups would result in a much larger value for $B - C$. The nitrosyl and carbonyl groups form different angles with the z-axis which passes through the Cr atom and center of C_5H_5. The C_5H_5–Cr–NO angle is 128°, and the C_5H_5–Cr–CO angle is 120°. The distance from the Cr atom to the C_5H_5 ring is z (Cr–C_5H_5) = 1.86 Å. The a-axis forms an angle of 4° with the z-axis. Other structural parameters are obtained and discussed. The C_5H_5 ring is oriented so that two of the cyclopentadienyl carbon atoms are staggered with respect to the NO nitrogen atom. The ^{14}N quadrupole coupling values are $eQq_{aa} = 0.312(2)$ and $eQq_{bb} = -0.448(2)$ MHz.

Introduction

The (η^5-C_5H_5)$Cr(CO)_2NO$ complex provides an opportunity to compare structural parameters of the nitrosyl and carbonyl ligands in a simple piano-stool-type complex. A large variety of diamagnetic metal–nitrosyl complexes have been studied,[1,2] with the M–N–O geometry ranging from linear to strongly bent. There has been renewed interest in NO complexes recently since NO was found to be a neurotransmitter.[3]

Some structural parameters were obtained from an X-ray diffraction study[4] of cyclopentadienylchromium dicarbonyl nitrosyl, but since the crystals were disordered with respect to nitrosyl and carbonyl positions, no comparative data on these ligands could be obtained. Structural parameters from the related fluorenylchromium dicarbonyl nitrosyl complex[4] were helpful in the present work. The result that this complex is very close to being a prolate symmetric top was initially unexpected and clearly indicates significant differences in the Cr–NO and Cr–CO structural parameters.

Experimental Section

Microwave spectra in the 4–12 GHz range were measured using a Flygare-Balle type spectrometer[5] equipped with a heated-nozzle, pulsed-beam source. The solenoid pulse valve (General Valve 9-181) and sample cell were maintained at 36–42 °C to provide sufficient sample vapor pressure. The sample was cooled using first-run neon (Airco) at 0.5 –1.0 atm as the expansion gas.

The signal-to-noise ratio for a-dipole transitions was about a factor of 10 higher than for b-dipole transitions. Spectra for the a-dipole transitions of ^{13}C isotopomers were readily observed, in natural abundance, for the normal isotopic sample and for the ^{15}NO substituted sample. Transitions were stronger and more easily measured for the ^{15}NO sample, since there was no ^{14}N quadrupole hyperfine splitting.

The normal isotope distribution sample of (η^5-C_5H_5)$Cr(CO)_2NO$ was synthesized by following the procedure given by Chin *et al.* in ref 6. Reflux times were cut to 6–8 h to reduce thermal decomposition of the intermediate product, Na[(η^5-C_5H_5)$Cr(CO)_3$]. The washing steps were omitted, but remaining dibutyl ether and $Cr(CO)_6$ were removed by sublimation at 90 °C, 0.005 Torr. Following addition of the THF–Diazald solution, and solvent removal, the product was sublimed onto a column with a temperature gradient (0–27 °C) to facilitate separation of the product from a yellow-white impurity (presumably from the Diazald). Bright red crystals of cyclopentadienyl chromium dicarbonyl nitrosyl were obtained. The IR spectrum showed strong CO peaks at 1944.5 and 2019.7 cm^{-1} and a strong NO peak at 1693.7 cm^{-1}, in agreement with previous values.[6] A weak absorption at 2930 cm^{-1} is assigned to C–H modes in the cyclopentadienyl group. This spectrum was obtained from a thin film of sample deposited on a salt plate by evaporation of the THF solvent.

The ^{15}NO-substituted sample was prepared from [(η^5-C_5H_5)$Cr(CO)_3$]$_2$ by following the procedure described by Fischer and Plesske.[7] Due to the high cost of the ^{15}NO (Isotec, Inc.), the ^{15}NO was placed in a closed 250 mL flask at 1 atm pressure for 24 h rather than bubbling the NO through the solution. The concentrated solution of the $C_5H_5Cr(CO)_3$ dimer in benzene (20 mL) was placed in the bottom of the closed 250 mL flask and stirred vigorously. The dark green solution gradually changed to orange-brown as the dimer was converted to $C_5H_5Cr(CO)_2NO$. The procedure for preparation of the $C_5H_5Cr(CO)_3$ dimer from NaC_5H_5 and $Cr(CO)_6$ with allyl bromide addition is described by King and Stone.[8] In the final step, the dimer was sublimed at 70 °C, 0.005 Torr onto a probe at 0 °C, for 3 days. The NaC_5H_5 was prepared as described in ref 9 and isolated as an off-white powder upon removal of the THF.

Data Analysis and Rotational Constants

The measured transition frequencies and those calculated using a least-squares fit for the normal isotopomer are listed in

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Table 1. Measured and Calculated Rotational Transition Frequencies for $C_5H_5Cr(CO)_2NO$[a]

J	K_p	K_o	F	J'	K_p'	K_o'	F'	measd	calcd	diff
2	1	2	3	3	1	3	4	4782.450	4782.460	−0.010
2	0	2	3	3	0	3	4	4782.849	4782.847	0.002
2	1	1	3	3	1	2	4	4783.220	4783.227	−0.007
2	1	1	2	3	1	2	3	4783.265	4783.258	0.007
2	1	2	3	3	2	1	4	5396.878	5396.877	0.001
2	2	0	3	3	3	1	4	5805.600	5805.600	0.000
3	1	3	2	4	0	4	3	6173.280	6173.281	−0.001
3	1	3	4	4	0	4	5	6173.316	6173.315	0.001
3	1	3	3	4	0	4	4	6173.440	6173.440	−0.001
3	1	3	4	4	1	4	5	6376.606	6376.608	−0.002
3	2	2	2	4	2	3	3	6377.093	6377.105	−0.012
3	0	3	4	4	0	4	5	6377.125	6377.122	0.003
3	1	2	4	4	1	3	5	6377.642	6377.636	0.006
3	0	3	3	4	1	4	4	6580.304	6580.302	0.003
3	0	3	4	4	1	4	5	6580.412	6580.415	−0.002
3	0	3	2	4	1	4	3	6580.456	6580.453	0.003
3	1	2	3	4	2	3	4	6989.890	6989.899	−0.009
3	1	2	4	4	2	3	5	6990.034	6990.032	0.003
3	1	3	4	4	2	2	5	6991.535	6991.535	0.000
3	1	3	3	4	2	2	4	6991.602	6991.598	0.004
3	2	1	4	4	3	1	5	7399.876	7399.875	0.001
4	1	4	3	5	0	5	4	7768.067	7768.071	−0.004
4	1	4	5	5	0	5	6	7768.105	7768.095	0.009
4	1	4	4	5	0	5	5	7768.210	7768.212	−0.002
3	3	0	3	4	4	0	4	7808.923	7808.935	−0.012
3	3	0	4	4	4	0	5	7808.953	7808.954	0.000
4	1	4	5	5	1	5	6	7970.750	7970.747	0.003
4	0	4	5	5	0	5	6	7971.387	7971.388	−0.001
4	1	3	5	5	1	4	6	7972.042	7972.034	0.008
4	0	4	5	5	1	5	6	8174.029	8174.039	−0.010
4	0	4	3	5	1	5	4	8174.078	8174.067	0.011
4	1	3	3	5	2	4	4	8583.820	8583.819	0.001
4	1	4	5	5	2	3	6	8586.322	8586.320	0.002
4	1	4	4	5	2	3	5	8586.387	8586.395	−0.008
4	2	2	5	5	3	3	6	8994.148	8994.143	0.006
4	3	1	5	5	4	2	6	9403.229	9403.223	0.006
5	1	5	6	6	1	6	7	9564.882	9564.876	0.006
5	2	4	6	6	2	5	7	9565.650	9565.656	−0.006
5	1	4	5	6	1	5	6	9566.431	9566.427	0.003
4	4	0	5	5	5	0	6	9812.287	9812.288	−0.001
6	1	6	7	7	1	7	8	11158.995	11158.992	0.002
6	2	5	7	7	2	6	8	11159.902	11159.909	−0.006
6	1	5	6	7	1	6	7	11160.798	11160.801	−0.003

[a] The calculated values were obtained using least-squares fit variables given in Table 2. The listed quantum numbers are J—rotational angular momentum, K_p—value of K prolate, K_o—value of K oblate, and F—the total angular momentum. The a-dipole transitions have $\Delta K_p = 0$ and b-dipole have $\Delta K_p = \pm 1$. Values are in MHz; the standard deviation for the fit is 0.006 MHz.

Table 1. There are 17 *a*-dipole and 26 *b*-dipole transitions listed. Although the *b*-dipole transitions were weaker, the ^{14}N quadrupole hyperfine structure was better resolved. Four observed transitions were not included in the fit due to unresolved hyperfine structure and ambiguities in assignments of quantum numbers. The total angular momentum quantum number F is obtained from the vector coupling scheme $\vec{F} = \vec{I} + \vec{J}$, where I is the ^{14}N nuclear spin. The matrix elements for the nitrogen quadrupole coupling were given earlier.[10] The molecular parameters obtained by fitting the observed transitions are listed in Table 5. Attempts were made to assign the 26 *b*-dipole transitions as *c*-dipole transitions, but no acceptable fits could be obtained. Since the dipole moment components must lie in the plane of symmetry of this complex, which contains the NO group, the *a* and *b* principal axes must also lie in this plane of symmetry. It is important to establish the *b* principal axis direction because the *B* and *C* rotational constants are so close in value; small changes in structural parameters would cause the *b* and *c* principal axis directions to interchange.

The isotopomers with ^{13}C or ^{15}N substitution have $B - C$ values which are a factor of 10, or more, larger than $B-C$ for the normal isotopomer, so the splitting of different K-states is larger and the spectra are more easily assigned and not as congested. Rotational constants for the different possible ^{13}C substitutions on the cyclopentadienyl ring carbons, however, are not very different, so only spectra for two of the possible three unique cyclopentadienyl ring ^{13}C isotopomers were unambiguously assigned. This complex has a mirror plane, formed by the *a* and *b* inertial axes of the normal isotopomer, so the pairs of substitution sites not located on this plane will have the same rotational constants. The ^{13}CO isotopomer, with ^{13}C substitution on the carbonyl carbon, was readily assigned, without ambiguity. The measured *a*-dipole transition frequencies and deviations (measured − calculated) for single ^{13}C isotopic substitutions are listed in Table 2. Since only nine transitions are included for each isotopomer, the ^{14}N quadrupole coupling components were fixed at values obtained from the normal isotopomer (see Table 5). Since only *a*-dipole transitions are included, the uncertainties are much larger for the *A*-rotational constants than for *B* or *C*.

The measured and "best fit" calculated transition frequencies for 37 *a*- and *b*-dipole transitions for $C_5H_5Cr(CO)_2{}^{15}NO$ are listed in Table 3. The parameters obtained from the fit to the data are listed in Table 5. The *A*, *B*, and *C* rotational constants are determined with a precision of 2 ppm or better for the ^{15}NO data and for the normal isotopomer. The data and molecular parameters and transition frequencies for single ^{13}C isotopic substitution, ^{15}N isotopomers are listed in Tables 4 and 6. Again, insufficient data for the $^{13}C1$ isotopomer, which lies on the $a-c$ mirror plane of the molecule, were obtained to carry out a meaningful fit.

Structural Parameters

Rotational constants were obtained for eight isotopomers of cyclopentadienylchromium dicarbonyl nitrosyl by fitting the measured transition frequencies. Since only *a*-dipole transitions

Table 2. Measured and Measured − Calculated (diff) Frequencies for Single ^{13}C Substitution Isotopomers of $C_5H_5Cr(CO)_2NO$[a]

								^{13}CO		$^{13}C2$		$^{13}C3$	
J	K_p	K_o	F	J'	K_p'	K_o'	F'	measd	diff	measd	diff	measd	diff
3	1	3	4	4	1	4	5	6348.441	−0.003	6334.130	0.002	6331.474	−0.004
3	0	3	4	4	0	4	5	6353.831	0.000	6337.325	0.000	6334.739	−0.001
3	1	2	4	4	1	3	5	6359.679	0.000	6340.674	−0.001	6338.159	0.001
4	1	4	5	5	1	5	6	7935.494	0.002	7917.631	0.000	7914.321	0.002
4	0	4	5	5	0	5	6	7942.059	0.000	7921.574	0.002	7918.342	0.002
4	1	3	5	5	1	4	6	7949.537	0.002	7925.815	−0.002	7922.674	0.002
5	1	5	6	6	1	6	7	9522.498	0.001	9501.112	−0.001	9497.143	0.001
5	0	5	6	6	0	6	7	9530.136	0.000	9505.760	−0.001	9501.883	0.000
5	1	4	6	6	1	5	7	9539.342	−0.002	9510.940	0.003	9507.162	−0.003

[a] The fit parameters are given in Table 5, and the carbon atom numbering is shown in Figure 1. All listed transitions are *a*-dipole and in MHz frequency units.

Table 3. Measured and Calculated Rotational Transition Frequencies for $C_5H_5Cr^{15}NO(CO)^{13}CO$[a]

J	K_p	K_o	J'	K_p'	K_o'	measd	calcd	diff
2	1	2	3	0	3	4569.066	4569.067	−0.0013
2	0	2	3	1	3	4961.881	4961.881	0.0001
2	1	1	3	2	2	5371.964	5371.964	0.0002
2	1	2	3	2	1	5380.846	5380.845	0.0017
2	2	0	3	3	1	5782.058	5782.041	0.0169
3	1	3	4	0	4	6162.370	6162.370	0.0001
3	1	3	4	1	4	6351.090	6351.085	0.0049
3	0	3	4	0	4	6356.648	6356.649	−0.0009
3	2	2	4	2	3	6356.943	6356.943	0.0000
3	3	1	4	3	2	6357.024	6357.037	−0.0124
3	2	1	4	2	2	6357.249	6357.256	−0.0062
3	0	3	4	1	4	6545.362	6545.364	−0.0013
3	1	2	4	2	3	6956.833	6956.836	−0.0027
3	1	3	4	2	2	6974.753	6974.754	−0.0015
3	2	1	4	3	2	7371.213	7371.222	−0.0083
3	2	2	4	3	1	7371.384	7371.379	0.0047
4	1	4	5	0	5	7756.853	7756.851	0.0018
3	3	0	4	4	1	7777.019	7777.023	−0.0040
4	1	4	5	1	5	7938.787	7938.786	0.0006
4	0	4	5	0	5	7945.566	7945.565	0.0009
4	2	3	5	2	4	7946.119	7946.128	−0.0089
4	4	1	5	4	2	7946.307	7946.289	0.0180
4	2	2	5	2	3	7946.750	7946.752	−0.0024
4	1	3	5	1	4	7953.322	7953.323	−0.0017
4	0	4	5	1	5	8127.498	8127.501	−0.0028
4	1	3	5	2	4	8540.241	8540.247	−0.0065
4	1	4	5	2	3	8570.417	8570.421	−0.0043
5	1	5	6	1	6	9526.448	9526.443	0.0049
5	0	5	6	0	6	9534.336	9534.319	0.0164
5	2	4	6	2	5	9535.279	9535.278	0.0006
5	5	0	6	5	1	9535.546	9535.543	0.0024
5	2	3	6	2	4	9536.362	9536.368	−0.0059
5	1	4	6	1	5	9543.885	9543.881	0.0044
6	1	6	7	1	7	11114.048	11114.047	0.0016
6	0	6	7	0	7	11122.884	11122.881	0.0028
6	2	5	7	2	6	11124.375	11124.387	−0.0122
6	1	5	7	1	6	11134.377	11134.378	−0.0010

[a] The calculated values were obtained using least-squares fit variables given in Table 6. The *a*-dipole transitions have $\Delta K_p = 0$, and *b*-dipole have $\Delta K_p = \pm 1$. Values are in MHz; the standard deviation for the fit is 0.007 MHz.

were measured for all of the ^{13}C isotopomers, the *A* rotational constants for these isotopomers are much less accurate than other values and are not included in the fit to obtain structural parameters. The remaining 18 rotational constants are believed accurate to a few ppm (or better) and form a reasonably large data set for the structure fit. Previous experience with a number of transition metal complexes has indicated that bond lengths from neutron or X-ray diffraction crystal structures are in good agreement with gas-phase microwave data, whereas interbond angles may not be in agreement. We have, therefore, used some of the bond lengths from diffraction data as fixed parameters in the structure fit.

The X-ray crystal structures of cyclopentadienylchromium dicarbonyl nitrosyl and fluorenylchromium dicarbonyl nitrosyl were obtained by Atwood *et al.*[4] Since the NO and CO groups on the fluorenyl complex are not disordered, and the structural parameters would be expected to be quite similar to those of the cyclopentadienyl complex, we initially fixed C−O, N−O, Cr−C, and Cr−N bond lengths at those values obtained for the fluorenylchromium dicarbonyl nitrosyl complex. The Cr−C−O bond angles were fixed at 180°, since for a large number of metal carbonyls,[11] the M−C−O angles are within a few degrees of 180°. We initially fixed the C−C bond length at the value 1.383 Å obtained by Atwood *et al.*[4] for cyclopentadienylchromium dicarbonyl nitrosyl but found we could improve the fit to measured rotational constants using r(C−C) = 1.41*A* Å, an increase of 2.4%. The C−H bond length was fixed at 1.08 Å, the value obtained for cyclopentadiene.[12] In subsequent fits the Cr−CO and Cr−NO bond lengths were treated as adjustable parameters, but the fit was not improved significantly. We interpret this as an indication that the bond lengths do not change appreciably from the fluoroenyl to the cyclopentadienyl complex.

The results of the least-squares fit using the 18 measured rotational constants for eight isotopomers are given in Table 7. The adjustable and fixed parameters used in the fit are given in Table 8. There were seven freely adjustable parameters and the eighth, the C−C bond length, was constrained to 1.38 ± 0.04 Å, a range which includes values for many other cyclopentadienyl complexes. We believe that the difference between the z−Cr−N and z−Cr−CO angles is very well determined, since the values of $B - C$ for the various isotopomers are directly dependent on the difference between these angles. If these angles were the same we would have a $B - C$ value of approximately 6 MHz, rather than the observed value of 0.258 MHz, obtained for the normal isotopomer. We have assumed linear Cr−C−O bonding and observed the nearly linear Cr−N−O bonding indicated by the fourth parameter, Θ, in Table 8. We have assumed that the z-axis, which coincides with the cyclopentadienyl C_5 axis, passes through the center of the chromium atom. This implies that there is no "tilt" of the cyclopentadienyl group relative to the C_5H_5 center-of-mass−chromium axis.

Table 4. Measured and Measured − Calculated (diff) Frequencies for Double Substitution Isotopomers[a]

						^{13}CO		^{13}C2		^{13}C3	
J	K_p	K_o	J'	K_p'	K_o'	measd	diff	measd	diff	measd	diff
3	1	3	4	1	4	6328.221	−0.0009	6313.367	0.0002	6307.671	0.0005
3	0	3	4	0	4			6317.071	0.0002	6314.540	0.0006
3	2	2	4	2	3	6334.196	0.0019	6317.193	−0.0038	6314.984	−0.0064
3	3	0	4	3	1	6334.285	−0.0064				
3	2	1	4	2	2	6334.522	0.0026				
3	1	2	4	1	3	6340.081	0.0028	6320.990	0.0024	6322.177	−0.0001
4	1	4	5	1	5	7910.207	−0.0013	7891.673	−0.0007	7884.491	0.0014
4	0	4	5	0	5			7896.229	−0.0002	7892.807	0.0009
4	2	3	5	2	4			7896.470	0.0011	7893.657	−0.0034
4	2	2	5	2	3	7918.342	−0.0003			7894.616	0.0004
4	1	3	5	1	4	7925.026	0.0016	7901.200	0.0012	7902.618	0.0008
5	1	5	6	1	6	9492.150	0.0024	9469.959	0.0012	9461.245	0.0009
5	0	5	6	0	6	9500.156	0.0001			9470.829	−0.0009
5	2	4	6	2	5					9472.287	−0.0018
5	1	4	6	1	5	9509.918	−0.0025	9481.384	−0.0017	9482.988	0.0018

[a] The listed frequencies are for single ^{13}C substitutions in $C_5H_5Cr^{15}NO(CO)_2$. The fit parameters are given in Table 6. All listed transitions are *a*-dipole. Listed frequencies are in MHz.

Table 5. Molecular Parameters Obtained from the Least-Squares Fits to the Measured Transition Frequencies for the Normal and ^{13}C Isotopomers of $C_5H_5Cr(CO)_2NO$ Listed in Tables 1 and 2[a]

param	normal isotopomer	^{13}CO	$^{13}C2$	$^{13}C3$
A (MHz)	1001.693(2)	996.6(1)	1000.6(4.3)	996.7(3.8)
B (MHz)	797.2724(6)	795.6725(6)	792.6927(8)	792.9994(7)
C (MHz)	797.0143(6)	792.8625(6)	791.0215(8)	791.3614(7)
D_J (kHz)	0.08(1)	0.062(8)	0.059(1)	0.069(1)
D_{JK} (kHz)	−0.004(100)			
D_K (kHz)	0.16(8)			
eQq_{aa} (MHz)	0.312(2)	0.312 (fixed)	0.312 (fixed)	0.312 (fixed)
eQq_{bb} (MHz)	−0.448(2)	−0.448 (fixed)	−0.448 (fixed)	−0.448 (fixed)
σ(fit) (kHz)	6	2	2.4	2.7

[a] The listed error limits are 2σ. The nitrogen quadrupole coupling strengths for the ^{13}C isotopomers were fixed at the values obtained for the normal isotopomer.

Table 6. Molecular Parameters Obtained from the Least-Squares Fits to the Measured Transition Frequencies for the ^{15}N, and ^{15}N, ^{13}C Isotopomers of $C_5H_5Cr(CO)_2NO$ Listed in Tables 3 and 4[a]

param	value	^{13}CO, ^{15}NO	$^{13}C2$, ^{15}NO	$^{13}C3$, ^{15}NO
A (MHz)	997.487(2)	993.7(1.2)	995.5(4)	997(4)
B (MHz)	796.0765(9)	793.2607(9)	791.1929(4)	790.6407(6)
C (MHz)	793.1682(9)	790.2965(9)	790.2965	788.6995(6)
Δ_J (kHz)	0.07(1)	0.06(1)	0.064(6)	0.059(9)
Δ_{JK} (kHz)	−0.18(4)			
Δ_K (kHz)	0.2(1)			
σ(fit) (kHz)	7	3	1.7	3

[a] The listed error limits are 2σ. The nitrogen quadrupole coupling strengths for the ^{13}C isotopomers were fixed at the values obtained for the normal isotopomer.

Table 7. Results of the Fit-Determined Structural Parameters for $C_5H_5Cr(Co)_2NO$[a]

isotopomer	param	measd	calcd	diff
normal	A	1001.693	1001.705	−0.012
	B	797.272	797.288	−0.016
	C	797.014	797.034	−0.020
^{15}N	A	997.487	997.475	0.012
	B	796.077	796.087	−0.011
	C	793.168	793.162	0.006
^{13}CO	B	795.673	795.708	−0.036
	C	792.863	792.846	0.016
$^{13}C2$	B	792.693	792.681	0.012
	C	791.022	791.028	−0.006
$^{13}C3$	B	792.999	793.014	−0.015
	C	791.361	791.360	0.002
^{13}CO, ^{15}N	B	793.261	793.254	0.007
	C	790.297	790.292	0.004
$^{13}C2$, ^{15}N	B	791.193	791.174	0.019
	C	787.566	787.547	0.019
$^{13}C3$, ^{15}N	B	790.605	790.615	−0.011
	C	788.700	788.671	0.028

[a] The "best fit" parameters are listed in Table 8. Values are in MHz. σ(fit) = 21 kHz.

Table 8. Structural Parameters for Cyclopentadienylchromium Dicarbonyl Nitrosyl Obtained by Fitting the Rotational Constants for Eight Isotopomers (Table 9)[a]

adjustable interbond angles	designation	value (3σ) (deg)
z−Cr−N	α	128(1)
z−Cr−CO	β	120.1(5)
plane (zCO)$_1$ − plane (zCO)$_2$	γ	112.6(7)
Cr−N−O	Θ	176(4)

adjustable interatomic distances	value (3σ) (Å)
C_5H_5−Cr	1.86(2)
C1−C2	1.41(3)
Cr−N	1.69(1)
Cr−CO	1.88(1)

fixed bond lengths[4]	value (Å)
N−O	1.169
C−O	1.145
C1−H1	1.08

[a] Indicated error limits are 3σ. The z-axis is assumed to be perpendicular to the C_5H_5 ring and passes through the Cr atom. The C−C bond length was adjusted in steps over a limited range. D_{5h} symmetry was assumed for the C_5H_5 moiety.

Discussion

The structural parameters from the present work, and corresponding parameters from X-ray and neutron diffraction work[13−15] on similar complexes, are listed in Table 9. The Cr−Cp distance is quite well determined and in good agreement with the other values. This distance is correlated with the Cp, C−C, and C−H bond lengths, but the C−H bond length was fixed (1.08 Å) and our "best fit" C−C bond lengths are in excellent agreement with values in other, similar Cp complexes, such as the neutron diffraction results for $(Cp)_2MoH_2$.[13] The difference between the Cp−Cr−CO and Cp−Cr−NO angles for fluorenylchromium dicarbonyl nitrosyl[4] is slightly larger than the difference from the present work on $CpCr(CO)_2NO$. We believe that this difference in angles is very well determined in the present work. It is somewhat correlated with the nonlinearity of the Cr−N−O bonding, but the present results and data on two other complexes (Table 9) indicate that this bonding is nearly linear for these similar complexes. This near linearity of the Cr−N−O bonding is also supported by the relative small values of nitrogen quadrupole coupling values discussed below. The fixed bond lengths, r^*, taken from the (fluorenyl)$Cr(CO)_2NO$ work,[4] are in very good agreement with corresponding values for $CpCr(NO)_2Cl$ and $C_6H_6Cr(CO)_3$.

The angle between the planes formed by the z-axis and the two Cr−C−O bonds is γ = 113°. This is significantly different from 120°, which would be the value if the $Cr(CO)_2NO$ group had C_{3v} symmetry. This deviation from C_{3v} symmetry is also characterized by the OC−Cr−CO angles listed in Table 9. The deviation from C_{3v} symmetry is even greater for the fluorenyl complex.

The nitrogen quadrupole coupling strengths for various transition metal nitrosyl complexes[16,17] are listed in Table 10. All of the listed complexes are believed to have linear, or nearly

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Table 9. Comparison of the New Gas-Phase Structural Parameters with Similar Parameters Obtained Using Diffraction Methods[a]

		complex (ref no.)				
param	present work	$CpCrNO(CO)_2$ (4)	$FlCrNO(CO)_2$ (4)	$CpCr(NO)_2Cl$ (13)	$(Cp)_2MoH_2$ (14)	$C_6H_6Cr(CO)_3$ (15)
r(Cr−Cp)	1.86(2)	1.844(4)	1.884(5)	1.85(2)		
r(C1−C2)	1.41(3)	1.382(8)			1.421(5)	
r(Cr−N)	1.69(1)		1.687(7)	1.717(3)		
r(Cr−CO)	1.88(1)		1.864(4)			1.842(4)
∠Cp−Cr−N	128.(1)		128.5(5)	120.7(10)		
∠Cp−Cr−CO	120.1(5)		119.9(5)			127.1(8)
∠Cr−N−O	176(4)		179.9(7)	170.0(3)		
r*(N−O)	1.169		1.169(9)	1.158(4)		
r*(C−O)	1.145		1.145(6)			1.148(7)
∠OC−Cr−CO	92.0(7)		88.4(3)			87.4(7)

[a] Cp is used to denote η^5-C_5H_5. Bond lengths and distances r(A−B) are in Å; angles ∠A−B−C are in deg. r* indicates an assumed bond length. Fl denotes flourenyl (η^5-$C_{13}H_9$).

Table 10. Nitrogen Quadrupole Coupling Strengths (MHz) for Transition Metal−Nitrosyl Complexes[a]

	complex (ref no.)			
	$CpCr(CO)_2NO$[b]	$Fe(NO)_2(CO)_2$ (16)	$Co(CO)_3NO$ (17)	CpNiNO (18)
eQq_{aa}	0.312(2)	−0.79(3)	0.8	−1.22(1)
eQq_{bb}	−0.448(2)	0.27(3)	0.8	0.61
eQq_{cc}	0.136	0.52	−1.6(1)	0.61
eQq_{zz}		−1.5	−1.6	−1.2

[a] The z-axis is along the principal axis for the quadrupole coupling tensor. [b] Present work.

linear (180° ± 5°), nitrosyl bonding. The cobalt and nickel complexes are both symmetric tops, so the bonding is exactly linear, and the principal axis of the quadrupole coupling tensor corresponds with the unique inertial axis. The $CpCr(CO)_2$ and $Fe(NO)_2(CO)_2$ complexes are both asymmetric tops, and in both cases, the principal axis of the nitrogen quadrupole coupling tensor does not lie along the N−O bond direction. In the case of $Fe(NO)_2(CO)_2$, it is rotated 62° away from the N−O bond direction and lies in the plane of the *a* and *b* inertial axes. The identity of the *a* and *b* inertial axes, relative the M−N−O bonds, is approximately interchanged in $CpCr(CO)_2NO$ relative to $Fe(NO)_2(CO)_2$. If we compare eQq_{aa} ($CpCr(CO)_2NO$) with eQq_{bb} ($Fe(NO)_2(CO)_2$), and the corresponding eQ_{bb} and eQ_{aa} components, we see they have the same sign but have significant differences. Since no *b*-dipole transition data was obtained for ^{13}C isotopomers of $CpCr(CO)_2{}^{14}NO$, the principal axis components of eQq were not obtained for this complex. The angle between the Cr−N bond and the *a* principal axis is 57°, however, and this is very near the "magic angle", so if the N−O bond direction did coincide with the eQq_{zz} principal axis, we would expect eQq_{aa} to be near zero. Since it is not (eQq_{aa} = 0.312 MHz), we believe that the principal axis system for the nitrogen quadrupole coupling tensor is rotated by a significant amount (>20°) away from the N−O bond direction for this complex as well.

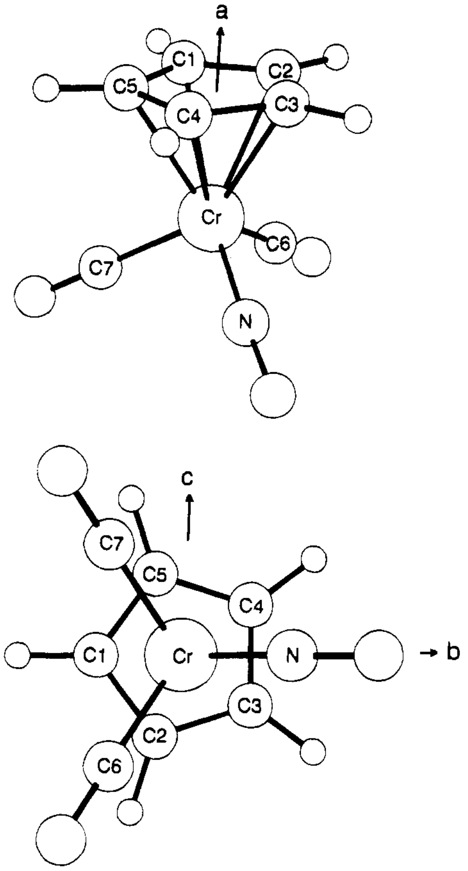

Figure 1. Two views of the (η^5-cyclopentadienyl)chromium dicarbonyl nitrosyl complex showing the relative orientation of C_5H_5 and $Cr(CO)_2NO$ fragments and the numbering of carbon atoms. C1 is the only unique carbon atom and lies on the molecular symmetry plane. The z-axis is coincident with the C_5 symmetry axis of the cyclopentadienyl group and passes through the Cr atom. The *a*−*c* principal rotational axes for the normal isotopomer are shown in the figure. The *a*-axis forms an angle of 4.3° with the z-axis.

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