the cobalt, nickel, and copper complexes (Table V) did not show any features that would indicate significant distortion of their coordination octahedra. The spectra were analyzed by assuming octahedral symmetry about the metal ions, and back-calculation of band positions from the best-fit values of *Dq* and *B* gave good agreement (less than 1.5% error for cobalt, less than 0.5% error for nickel) with the experimental band positions. The nickel complex displays the typical double ν_2 band associated with the mixing of the ^1E_g and $^3T_{1g}(F)$ energy levels. *Dq* values for the $M(pdcO)(H_2O)_2$ complexes are somewhat higher than those reported for six-coordinate complexes of various substituted pyridine *N*-oxides, most of which have *Dq* values in the ranges of 890–950 cm^{-1} for cobalt(II), 780–833 cm^{-1} for nickel(II), and 1220 cm^{-1} for copper(II).[3]

Ambient-temperature magnetic measurements (Table V) are consistent with six-coordination about the central metal ions and, with the exception of the 2.97 μ_B value for $Ni(pdcO)(H_2O)_2$, are consistent with values previously reported for six-coordinate complexes of other substituted pyridine *N*-oxides: 5.88–5.93 μ_B for manganese(II),[16,17] 4.71–4.84 μ_B for cobalt(II),[18] 3.30–3.34 μ_B for nickel(II),[18] and 1.91 μ_B for copper(II).[18] Manganese(II) complexes such as $Mn(py\text{-}N\text{-}O)Cl_2$ ((py-*N*-O) = pyridine *N*-oxide) for which chlorine-bridged structures are proposed have μ_{eff} values in the 5.40–5.60-μ_B range.[3] Monomeric copper(II) complexes with *N*-oxide ligands exhibit μ_{eff} values in the 1.75–2.04-μ_B range while dimeric copper(II) complexes have values as low as 0.22 μ_B resulting from strong spin–spin coupling.[19] A value of 0.85 μ_B has been reported for $Cu(py\text{-}N\text{-}O)Cl_2$, which is known to have an *N*-oxide-bridged dimeric structure.[20] Therefore, the μ_{eff} values for the $M(pdcO)(H_2O)_2$ complexes suggest no significant spin–spin coupling. The Mn–Mn′ separation of 4.011 (1) Å precludes any possibility of direct interaction between metal ions.

Typical of the other manganese(II) pyridine *N*-oxide complexes, $Mn(pdcO)(H_2O)_2$ is sensitive to visible light and its color changes over time from yellow to brown. Such changes have been attributed to a photooxidation–photoreduction process that produces manganese(III) and the parent amine.[21]

Acknowledgment. The authors thank the Chemistry Department, San Jose State University, for the use of their XRD-8000 instrument.

Registry No. $Mn(pdcO)(H_2O)_2$, 97277-46-8; $Co(pdcO)(H_2O)_2$, 97277-47-9; $Ni(pdcO)(H_2O)_2$, 97277-48-0; $Cu(pdcO)(H_2O)_2$, 97277-49-1; $Zn(pdcO)(H_2O)_2$, 97277-50-4.

Supplementary Material Available: A listing of observed and calculated structure factors, a table of anisotropic thermal parameters, and a stereoview of the unit cell of $[Mn(pdcO)(H_2)_2]_n$ (5 pages). Ordering information is given on any current masthead page.

---

(16) Carlin, R. L. *J. Am. Chem. Soc.* **1961**, *83*, 3773.

(17) Byers, W.; Lever, A. B. P.; Parish, R. V. *Inorg. Chem.* **1968**, *7*, 1835.

(18) Whyman, R.; Hatfield, W. E.; Paschal, J. S. *Inorg. Chim. Acta* **1967**, *1*, 113.

(19) Watson, W. H. *Inorg. Chem.* **1969**, *8*, 1879.

(20) Sager, R. S.; Williams, R. J.; Watson, W. H. *Inorg. Chem.* **1967**, *6*, 951.

(21) Nathan, L. C.; Cullen, J.; Ragsdale, R. O. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 137.

Contribution from the Departments of Chemistry, Oregon State University,
Corvallis, Oregon 97331, and University of Texas, Austin, Texas 78712

Structure and Bonding in Transition-Metal Carbonyls and Nitrosyls. 1. Gas-Phase Electron Diffraction Investigations of Tetranitrosylchromium ($Cr(NO)_4$), Carbonyltrinitrosylmanganese ($MnCO(NO)_3$), and Dicarbonyldinitrosyliron ($Fe(CO)_2(NO)_2$)

LISE HEDBERG,[1a] KENNETH HEDBERG,*[1a] SUSHIL K. SATIJA,[1b] and BASIL I. SWANSON[1c]

Received October 26, 1984

The molecular structures of gaseous $Cr(NO)_4$, $MnCO(NO)_3$, and $Fe(CO)_2(NO)_2$ have been investigated by electron diffraction at nozzle-tip temperatures of 29–37, 19–30, and 23 °C, respectively. The molecules have tetrahedral coordination, and the data are in each case completely consistent with linear M–Y–O groups. Values for the bond lengths (r_g) and bond angles ($\angle_\alpha$) with estimated 2σ uncertainties are as follows: for $Cr(NO)_4$, $r(\mathrm{Cr{-}N}) = 1.763$ (2) Å, $r(\mathrm{N{=}O}) = 1.171$ (2) Å (T_d symmetry assumed); for $MnCO(NO)_3$, $r(\mathrm{Mn{-}N}) = 1.717$ (2) Å, $r(\mathrm{Mn{-}C}) = 1.947$ (7) Å, $r(\mathrm{N{=}O}) = 1.167$ (2) Å, $r(\mathrm{C{=}O}) = 1.145$ (6) Å, $\angle\mathrm{NMnN} = 112.5$ (43)°, $\angle\mathrm{CMnN} = 106.2$ (49)° (C_{3v} symmetry assumed); for $Fe(CO)_2(NO)_2$, $r(\mathrm{Fe{-}N}) = 1.688$ (3) Å, $r(\mathrm{Fe{-}C}) = 1.883$ (3) Å, $r(\mathrm{N{=}O}) = 1.171$ (4) Å, $r(\mathrm{C{=}O}) = 1.140$ (4) Å, $\angle\mathrm{NFeN} = 114.2$ (62)°, $\angle\mathrm{CFeN} = 108.4$ (13)°, $\angle\mathrm{CFeC} = 110.2$ (25)° (C_{2v} symmetry assumed). These compounds, together with $Co(CO)_3NO$ and $Ni(CO)_4$ studied earlier, comprise a series of five isoelectronic molecules that allows unusual insight into the nature of the bonding between transition metals and nitrosyl and carbonyl ligands. Changes in bond lengths of the type Δr(M–C) and Δr(M–N) throughout the series are found to correspond to a generally increasing bond order in both cases as the atomic number of the metal increases, while at the same time the total bond order of the metal bonds in each compound changes very little. These metal–ligand bond order changes are interpreted in terms of a redistribution of $d\pi$–π^* back-bonding and, together with the M–Y distances themselves, are consistent with the NO ligand being a much better electron acceptor than the CO ligand.

Introduction

The nature of the bonding between transition-metal atoms and ligands such as CO and NO is a matter of considerable current interest. These bonds are usually regarded as having a σ component arising from donation of an unshared electron pair on the carbon or nitrogen atom and a "back-bonding" π component arising from combination of an appropriate filled metal orbital with an antibonding orbital on the ligand. The interesting questions concern the relative amounts of the two bond components and the relative abilities of CO and NO to participate in back-bonding. Information bearing on these questions includes bond strengths, charge distributions, and molecular structure as deduced from a variety of experiments and from theoretical calculations.

One approach to an understanding of the bonding in the transition-metal carbonyls and nitrosyls involves comparisons of

---

(1) (a) Oregon State University. (b) University of Texas. Present address: Physics Department, University of Delaware, Newark, DE 19711. (c) University of Texas. Present address: University of California, Los Alamos Scientific Laboratory, Los Alamos, NM 87545.

0020-1669/85/1324-2766$01.50/0

Table I. Experimental Conditions

	$Cr(NO)_4$		$MnCO(NO)_3$		$Fe(CO)_2(NO)_2$	
	long camera	middle camera	long camera	middle camera	long camera	middle camera
nozzle-to-plate distance/cm	75.07	30.07	75.07	30.07	75.07	30.07
exposure time/s	90	90–120	45–135	90–120	45–75	75–105
electron wavelength/Å[a]	0.056 66	0.056 67	0.056 59	0.056 64	0.056 60	0.056 60
beam current/μA	0.30	0.30–0.32	0.30	0.32	0.26–0.30	0.30
ambient apparatus press./torr × 10^6	3.0	3.7–6.0	2.3–3.0	5.6–5.8	3.4	3.8–4.0
no. of plates used	2	4	3	3	3	3
range of data/s[b]	2.00–12.75	6.00–31.00	1.00–12.75	5.00–31.00	1.00–12.75	5.00–31.00
data interval/s[b]	0.25	0.25	0.25	0.25	0.25	0.25
sample bath temp/°C	28	35	19	29	0	6
nozzle-tip temp/°C	29	37	19	30	23	23

[a] From voltage calibrations in separate experiments against CO_2: $r_a(CO) = 1.1646$ Å, $r_a(OO) = 2.3244$ Å. [b] $s = 4\pi\lambda^{-1}\sin\theta$; 2θ is the scattering angle.

properties, such as those mentioned above, of a series of closely related molecules. An especially attractive series for this purpose consists of $Ni(CO)_4$, $Co(CO)_3NO$, $Fe(CO)_2(NO)_3$, $MnCO(NO)_3$, and $Cr(NO)_4$. These isoelectronic molecules are each formally obtainable from adjacent members by transfer of a single proton between metal and ligand nuclei. Moreover, each substance is volatile enough to allow its study in the gaseous state, where the properties of interest are least perturbed by intermolecular interaction. Unfortunately, the thermal stability of the compounds decreases markedly as the number of NO groups increases so that few measurements have been made on $Fe(CO)_2(NO)_2$, $MnCO(NO)_3$, and particularly $Cr(NO)_4$. Among these are X-ray photoelectron spectra[2] (for all five molecules). Important conclusions about the bonding are derived from the core binding energies, and we shall turn to these in the discussion of our own results. Other results include force constants for $Ni(CO)_4$,[3] $Co(CO)_3NO$,[4] and $Fe(CO)_2(NO)_2$,[5] ionization potentials[6] and charge distributions[6] for these molecules, and bond lengths for $Ni(CO)_4$.[3a]

Our interest in the bonding and structural features of simple transition-metal carbonyl nitrosyl complexes has led us to investigations of the five molecules discussed above by gaseous electron diffraction. The $Ni(CO)_4$ work has been reported,[3a] and the $Co(CO)_3NO$ work is described in the following article.[7] This article is an account of our results for the iron, manganese, and chromium compounds. Aside from some imprecise (by modern standards) bond lengths for $Fe(CO)_2(NO)_2$,[8] no structure data from diffraction have been obtained for these compounds.

Experimental Section

Materials, Methods, and Data Reduction. $Fe(CO)_2(NO)_2$ was prepared according to the method of Heiber and Beutner,[9] and $MnCO(NO)_3$ and $Cr(NO)_4$ were prepared according to that of Swanson and Satija.[10] Each product was vacuum sublimated, after which its IR spectrum indicated it to be essentially pure.

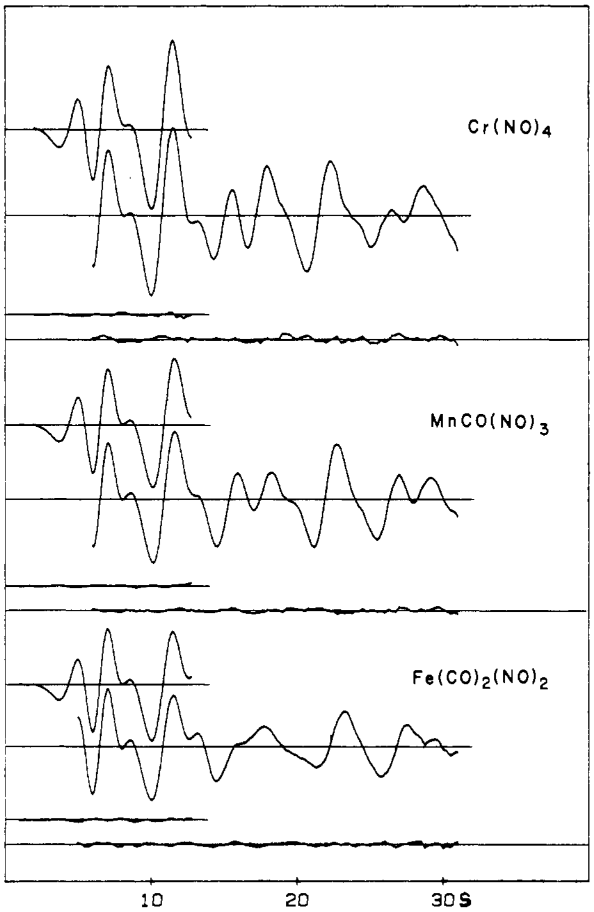

Figure 1. Molecular intensity curves. The oscillating curves are the averages of experimental data from the long and intermediate camera distances. The lower pairs are the differences (experimental minus theoretical) for the models of Table III.

Diffraction photographs were made in the Oregon State apparatus using an r^3 sector and 8 × 10 in. Kodak projector slide plates (medium contrast) developed for 10 min in Kodak D-19 diluted 1:1. During the experiments, the bulk samples were kept at as low a temperature as possible sufficient for development of adequate vapor pressure. The nozzle tip was at room temperature or, when necessary to prevent condensation, a few degrees higher than the sample bath. $Cr(NO)_4$ is unstable at the bath temperatures required for it, and during the course of the experiment, a thin film of chromium metal appeared on the walls of the glass sample bulb. Very slight decomposition was also observed in the case of $MnCO(NO)_3$. Table I summarizes details of the conditions of the experiments.

The procedures for reduction of the data to yield the total leveled intensities s^4I_t have been described.[11] Calculated backgrounds[12] were subtracted to yield a set of molecular intensity data $sI_m(s)$ from each plate. The data were combined into average sets from each camera distance for each molecule. Curves of these averages are shown in Figure 1. The leveled total intensities from each plate, the corresponding backgrounds, and the averaged data are available as supplementary material.

---

(2) Chen, H.-W.; Jolly, W. L. *Inorg. Chem.* **1979**, *18*, 2548.

(3) (a) Hedberg, L.; Iijima, T.; Hedberg, K. *J. Chem. Phys.* **1979**, *70*, 3224. (b) Jones, L. H.; McDowell, R. S.; Goldblatt, M. *J. Chem.* **1968**, *48*, 2663.

(4) (a) Jones, L. H.; McDowell, R. S.; Swanson, B. I. *J. Chem. Phys.* **1973**, *58*, 3757. (b) Mann, R. H.; Hyams, I. J.; Lippencott, E. R. *J. Chem. Phys.* **1968**, *48*, 4929.

(5) Poletti, A.; Santucci, A.; Foffani, A. *J. Mol. Struct.* **1969**, *3*, 311.

(6) Hillier, I. H.; Guest, M. F.; Higgenson, B. R.; Lloyd, D. R. *Mol. Phys.* **1974**, *27*, 215.

(7) Hedberg, L.; Hedberg, K.; Hagen, K.; Ryan, R. R.; Jones, L. H. *Inorg. Chem.*, following paper in this issue.

(8) Brockway, L. O.; Anderson, J. S. *Trans. Faraday Soc.* **1937**, *38*, 1233.

(9) Hieber, W.; Beutner, H. *Z. Anorg. Allg. Chem.* **1963**, *320*, 101. See also: King, R. B. *Organomet. Synth.* **1965**, *1*, 167.

(10) Swanson, B. I.; Satija, S. K. *J. Chem. Soc., Chem. Commun.* **1973**, 40.

(11) Gundersen, G.; Hedberg, K. *J. Chem. Phys.* **1969**, *51*, 2500.

(12) Hedberg, L. "Abstracts of Papers", Fifth Austin Symposium on Gas-Phase Molecular Structure, Austin, TX, March, 1974; No. T9.

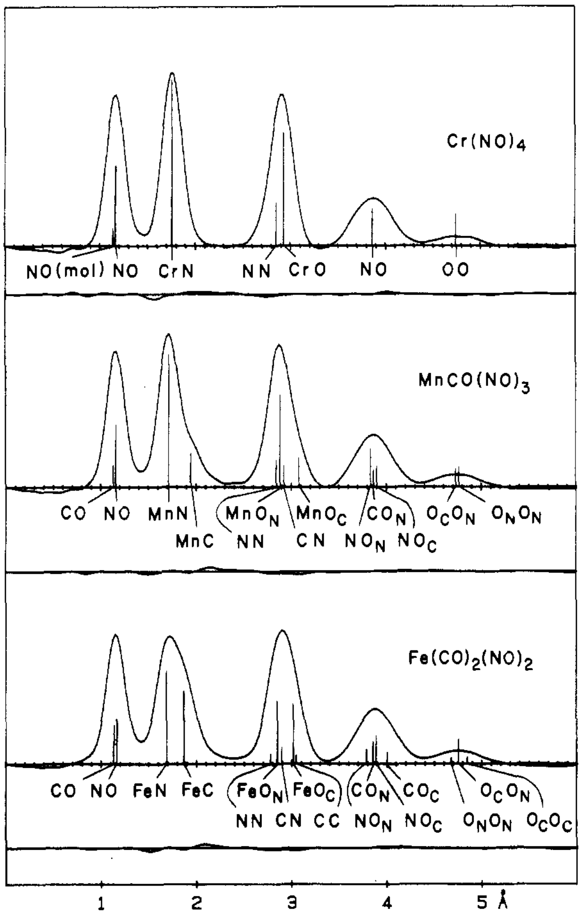

Figure 2. Radial distribution curves. Distances and their relative weights are shown by vertical bars below the experimental curves. The difference curves are experimental minus theoretical.

Intensity and Radial Distribution Calculations. The intensity and radial distribution calculations required for the structure analyses were based on the functions

$$sI_m(s) = k\sum_{i\neq j} A_iA_jr_{ij}^{-1}\exp(-l_{ij}^2s^2/2)\cos(\eta_i - \eta_j)\sin sr_{ij} \quad (1)$$

$$rD(r) = (2/\pi)\Delta s\sum_{s_{min}}^{s_{max}} sI_m(s)Z_MZ_OA_M^{-1}A_O^{-1}\exp(-Bs^2)\sin sr \quad (2)$$

The modified scattering amplitudes $A(s) = s^2|F|$ and phases η were obtained from tables.[13] The experimental $rD(r)$ curves (Figure 2) were calculated from composites of the experimental intensity averages mentioned above; data for the unobserved or uncertain region $s \leq 2.00$ Å^{-1} were taken from theoretical curves. In most calculations the convergence coefficient B was given the value 0.0025 Å^2.

Structure Analyses

Preliminary radial distribution curves were easily interpreted to give trial structures suitable for refinement. As expected, the curve for $Cr(NO)_4$ is consistent with a tetrahedral molecule and those for $MnCO(NO)_3$ and $Fe(CO)_2(NO)_2$ are consistent with molecules of respective symmetries C_{3v} and C_{2v} having bond angles at the metal atoms only slightly different from the tetrahedral value. The curves give no evidence for nonlinearity of the MCO and MNO groups.

Vibrational Corrections. In order to improve the chances of detecting small differences in the parameter values of the molecules, it was thought best to define the structures for refinement in terms of r_α bond lengths and bond angles: unlike r_a parameters, this type leads to nonbond distances consistent with restrictions imposed by overall geometry.[14] Since r_a distances are required for calculations of scattered intensities (eq 1), the $r_a - r_\alpha$ differences had to be estimated. These are given by

$$r_a - r_\alpha = r_g - r_\alpha - l^2/r_\alpha = K + \delta r - l^2/r_\alpha \quad (3)$$

Table II. Parameter Values for Final Models[a]

param	$Cr(NO)_4$	param	MnCO-$(NO)_3$	$Fe(CO)_2$-$(NO)_3$
$r_\alpha(N{=}O)$	1.152 (2)	$\langle CO,NO\rangle^b$	1.143 (2)	1.137 (2)
$r_\alpha(Cr{-}N)$	1.750 (2)	$\Delta(CO,NO)^c$	−0.022 (8)	−0.031 (7)
$\chi(NO)^d$	0.43 (7)	$\langle MC,MN\rangle^b$	1.762 (2)	1.773 (2)
R^e	0.057	$\Delta(MC,MN)^c$	0.232 (6)	0.198 (3)
		$\langle CFeC,NFeN\rangle^f$		112.2 (25)
		$\Delta(CFeC,NFeN)^g$		[4.0] (80)
		$\angle_\alpha CFeC$		110.2 (25)
		$\angle_\alpha CMN$	106.2 (49)	108.4 (13)
		$\angle_\alpha NMN$	112.5 (43)	114.2 (62)
		$\chi(NO)^d$	0.14 (11)	
		R^e	0.045	0.053

[a] Distances in angstroms; angles in degrees. [b] Number average of distances. [c] First distance minus second. [d] Mole fraction of nitric oxide. [e] $R = \sum w_i[sI(\text{obsd}) - sI(\text{calcd})]_i^2/\sum w_i[sI(\text{obsd})]_i^2$. [f] Average angle. [g] First angle minus second.

Although the mean-square amplitudes (l^2) are observable, the perpendicular amplitude corrections (K) and the centrifugal distortions (δr) are not and must be obtained by calculations based on vibrational force fields. The spectra of the chromium and manganese compounds from which force fields might be deduced have not been measured, and although a force field for the iron compound has been proposed,[5] later reassignments[15] of the spectrum make it of doubtful utility. In the absence of direct information about the values of $K + \delta r$ for our molecules, we decided to estimate them using values obtained from our extensive analysis of $Ni(CO)_4$[3] as a guide. The assumption of similar values for corresponding distance types in the chromium, manganese, iron, and nickel compounds is reasonable in view of the similar structures of the molecules and in any case hardly limiting because the $Ni(CO)_4$ values are quite small. To check the point we calculated $K + \delta r$ for $Co(CO)_3NO$, for which a good force field is available,[4] and for $Fe(CO)_2(NO)_2$ using a force field consistent with the ones for $Ni(CO)_4$ and $Co(CO)_3NO$ that gave a good fit to the observed,[5,15] reassigned[15] spectrum. The results suggest that errors introduced by adoption of the $Ni(CO)_4$ values are no larger than a few thousandths of an angstrom. The force field derived for $Fe(CO)_2(NO)_2$, the wavenumber fit it provides, and the symmetry coordinates on which it is based are available in the supplementary material. The values of $K + \delta r$ used in the structure refinements are listed in Table III.

Choice of Structural and Vibrational Parameters. Linear M—C≡O and M—N≡O groups and T_d, C_{3v}, and C_{2v} symmetry for the chromium, manganese, and iron compounds, respectively, were assumed. The structural parameters for $Cr(NO)_4$ were chosen to be the bond lengths $r_\alpha(Cr{-}N)$ and $r_\alpha(N{=}O)$. For the manganese and iron compounds convenient sets of distance parameters were found to be the weighted averages and the differences of similar types of distances: $\langle CO,NO\rangle = (nr_\alpha(C{=}O) + (4-n)r_\alpha(N{=}O))/4$ and $\Delta(CO,NO) = r_\alpha(C{=}O) - r_\alpha(N{=}O)$, with corresponding definitions for $\langle MC,MN\rangle$ and $\Delta(MC,MN)$. There is one angle parameter in the manganese compound, taken to be $\angle_\alpha$C-Mn-N. For the two angle parameters in $Fe(CO)_2(NO)_2$ we again found the average, $\langle CFeC,NFeN\rangle = (\angle_\alpha C\text{-}Fe\text{-}C + \angle_\alpha N\text{-}Fe\text{-}N)/2$, and the difference, $\Delta(CFeC,NFeN) = \angle_\alpha C\text{-}Fe\text{-}C - \angle_\alpha N\text{-}Fe\text{-}N$, to be convenient. There are 6 nonequivalent interatomic distances in $Cr(NO)_4$, 13 in $MnCO(NO)_3$, and 16 in $Fe(CO)_2(NO)_2$. The six vibrational amplitudes associated with the distances in $Cr(NO)_4$ could be refined independently, but in the other molecules their large numbers coupled with the lower molecular symmetries required that they be refined in groups. The groups were chosen to comprise largely amplitudes from distances of similar types found under a given peak of the radial distribution

---

(13) Schäfer, L.; Yates, A. C.; Bonham, R. A. *J. Chem. Phys.* **1971**, *55*, 3056.

(14) Morino, Y.; Kuchitsu, K.; Oka, T. *J. Chem. Phys.* **1962**, *36*, 1108.

(15) Paliani, G.; Cataliotti, R.; Poletti, A. *Can. J. Spectrosc.* **1976**, *21*, 159.

Table III. Distances and Amplitudes for Final Models[a]

	Cr(NO)$_4$		MnCO(NO)$_3$		Fe(CO)$_2$(NO)$_2$		
	r_g/Å	l/Å	r_g/Å	l/Å	r_g/Å	l/Å	$(K + \delta r)$/Å[b]
C=O			1.145 (6)	0.033 } (3)	1.140 (4)	0.040 } (3)	0.019
N=O	1.171 (2)	0.042 (3)	1.167 (2)	0.036	1.171 (4)	0.043	0.019
M–C			1.949 (7)	0.051 } (3)	1.883 (3)	0.057 } (3)	0.013
M–N	1.763 (2)	0.054 (3)	1.717 (2)	0.046	1.688 (3)	0.052	0.013
M·O$_C$			3.083 (7)	0.053 } (4)	3.013 (5)	0.057 } (6)	0.021
M·O$_N$	2.923 (4)	0.063 (4)	2.873 (3)	0.055	2.848 (5)	0.059	0.021
C·C					3.078 (49)	0.099	0.009
C·N			2.923 (94)	0.098 } (29)	2.881 (23)	0.099	0.009
N·N	2.866 (4)	0.123 (17)	2.844 (69)	0.098	2.822 (99)	0.099	0.009
C··O$_C$					4.053 (57)	0.162 } (13)	0.013
C··O$_N$			3.881 (117)	0.174 } (13)	3.856 (30)	0.162	0.013
N··O$_C$			3.911 (110)	0.174	3.869 (26)	0.162	0.013
N··O$_N$	3.869 (5)	0.190 (16)	3.856 (87)	0.174	3.845 (121)	0.162	0.013
O$_C$···O$_C$					4.921 (74)	0.243 } (37)	0.013
O$_C$···O$_N$			4.744 (150)	0.258 } (43)	4.724 (38)	0.243	0.013
O$_N$···O$_N$	4.752 (6)	0.277 (74)	4.758 (120)	0.258	4.761 (164)	0.243	0.013

[a] Values in parentheses are estimates of 2σ; braces indicate amplitudes refined in groups. [b] Estimated $r_g - r_\alpha$ corrections; see eq 3.

Table IV. Correlation Matrix (×100) for Cr(NO)$_4$

	σ[a]	r_1	r_2	χ	l_1	l_2	l_3	l_4	l_5	l_6
r(N=O)	0.067	100	-22	51	29	-24	<1	-42	-7	-5
r(Cr—N)	0.053		100	-3	-3	-4	15	-25	1	<1
χ(NO)[b]	2.62			100	60	-41	-18	-46	-15	-9
l(N=O)	0.101				100	4	7	-13	-1	-2
l(Cr—N)	0.080					100	26	36	14	7
l(Cr·O)	0.108						100	-18	9	3
l(N·N)	0.563							100	12	4
l(N·O)	0.492								100	-27
l(O·O)	2.596									100

[a] Standard deviations from least squares (×100); in angstroms for distances and amplitudes. [b] Mole fraction of free nitric oxide.

Table V. Correlation Matrix (×100) for MnCO(NO)$_3$

	σ[a]	$\langle r_1\rangle$	Δr_1	$\langle r_2\rangle$	Δr_2	$\angle_1$	$\angle_2$	χ	l_1	l_2	l_3	l_4	l_5	l_6
⟨CO,NO⟩	0.038	100	-34	-19	17	-2	2	17	25	-3	11	<1	2	-3
Δ(CO,NO)	0.275		100	7	-46	-18	18	6	-33	6	-26	21	5	-3
⟨MnC,MnN⟩	0.055			100	-68	-24	24	-20	-2	26	27	20	21	-3
Δ(MnC,MnN)	0.198				100	15	-15	11	6	-35	-20	-11	-14	1
∠CMnN	172.6					100	-100	1	5	-5	-11	-93	-59	25
∠NMnN	150.4						100	-1	-5	5	11	93	59	-25
χ(NO)[b]	3.82							100	47	-35	-13	-13	-16	-10
l(C=O)[c]	0.079								100	22	14	-5	1	1
l(Mn—C)[c]	0.064									100	21	14	18	8
l(Mn·O$_C$)[c]	0.098										100	-6	13	-1
l(C·N)[c]	1.002											100	59	-21
l(C··O$_N$)[c]	0.367												100	-30
l(O$_C$··O$_N$)[c]	1.467													100

[a] Standard deviations from least squares (×100); in angstroms for distances and amplitudes and in degrees for angles. [b] Mole fraction of free nitric oxide. [c] Amplitude groups are identified by the first member of each group.

curve. The fixed differences between amplitudes in a given group were estimated in the manner described for estimation of $K + \delta r$. This procedure led to six group amplitude parameters for the manganese compound and five for the iron. The composition of the groups is seen in Table III. Because of the evident decomposition of Cr(NO)$_4$, and to a lesser extent MnCO(NO)$_3$, during the diffraction experiments, a composition parameter indicative of the amount of NO present was introduced in each case. The bond length and vibrational amplitude of NO were taken from the literature.[16]

Results. The refinements were carried out by least-squares techniques[17] fitting an intensity curve in the form of eq 1 to the two average curves for each molecule. The results are given in Tables II and III. Correlation matrices for the more important parameters are given in Tables IV–VI.

The refinements for the chromium and manganese compounds proceeded smoothly to convergence with no restrictions other than those already described. In the case of the iron compound, however, it was not possible to refine the parameter Δ(CFeC,NFeN). Tests with this parameter set at values in the range 4–12° gave about the same overall agreement with experiment and led to almost the same bond lengths. The NFeN and CFeN angles, too, were little affected, but the CFeC angle changed over a 6° range. We also explored, in the case of the iron compound, the effect of the assumptions concerning the differences assigned to members of the group of amplitudes associated with distances through one bond angle (Fe·O$_C$, Fe·O$_N$, etc). It was found that these differences between amplitudes involving the iron atom and the others of the group tended to be greater experimentally than the calculated values. Moreover, the structural parameters Δ(CO,NO) and ⟨CFeC,NFeN⟩ were found to be markedly affected by these amplitude differences, changing as much as 0.025 Å and 6° over the range of assumed differences comprising our tests. We have somewhat arbitrarily adopted a set of differences that

---

(16) r_g value calculated from r_e = 1.1508 Å (Gallegher, J. J.; Johnson, C. M. *Phys. Rev.* **1956**, *103*, 1727). Amplitude calculated from $\langle l^2\rangle = (h/8\pi^2\mu\nu)\coth(h\nu/2kT)$ with ν = 1876 cm^{-1} (Bhagavantam, S. *Phys. Rev.* **1932**, *42*, 437).

(17) Hedberg, K.; Iwasaki, M. *Acta Crystallogr.* **1964**, *17*, 529.

Table VI. Correlation Matrix (×100) for $Fe(CO)_2(NO)_2$

	σ[a]	$\langle r_1 \rangle$	Δr_1	$\langle r_2 \rangle$	Δr_2	$\langle \angle_1 \rangle$	$\Delta\angle_1$	$\angle_2$	$\angle_3$	$\angle_4$	l_1	l_2	l_3	l_4	l_5
⟨CO,NO⟩	0.040	100	2	−20	−2	4	−1	5	−4	1	10	11	3	2	−2
Δ(CO,NO)	0.241		100	−20	−52	34	64	−69	−36	55	52	−19	45	50	17
⟨FeC,FeN⟩	0.061			100	34	23	−3	27	−22	7	−14	8	1	−11	−14
Δ(FeC,FeN)	0.111				100	5	−6	14	−4	−2	−13	39	2	−4	−4
⟨CFeC,NFeN⟩	87.7					100	80	−31	−100	92	11	1	67	41	−5
Δ(CFeC,NFeN)	286.9						100	−81	−82	97	25	−6	78	67	15
∠CFeC	89.9							100	34	−65	−29	10	−59	−67	−28
∠CFeN	45.1								100	−93	−12	<1	−68	−43	4
∠NFeN	220.1									100	21	−4	77	60	8
$l(C{=}O)$[b]	0.071										100	24	29	30	10
$l(Fe{-}C)$[b]	0.076											100	13	2	−1
$l(Fe{\cdot}O_C)$[b]	0.164												100	56	11
$l(C{\cdot\cdot}O_C)$[b]	0.410													100	4
$l(O_C{\cdot\cdot}O_C)$[b]	1.260														100

[a] Standard deviations from least squares (×100); in angstroms for distances and amplitudes and in degrees for angles. [b] Amplitude groups are identified by the first member of each group.

are consistent with corresponding ones in the other compounds.

In view of the foregoing, we believe that the contents of Tables II and III comprise a reasonably accurate picture of the structures of $Cr(NO)_4$ and $MnCO(NO)_3$. In the case of $Fe(CO)_2(NO)_2$, however, the values of some of the parameters, particularly the differences between the lengths of the C=O and N=O bonds (but not their average), and the average value of the CFeC and the NFeN angles must be accepted with caution. The tabulated results for $Fe(CO)_2(NO)_2$ contain crude estimates of uncertainty in the nonrefinable parameter Δ(CFeC,NFeN) obtained by releasing all parameters allowing zero shifts. The effect of a change in the value of this parameter may be estimated by use of the correlation matrix.

Table VII. Bond Lengths, Bond Angles, and Bond Orders in Transition-Metal Carbonyl Nitrosyls[a]

	$Cr(NO)_4$[b]	$MnCO(NO)_3$[b]	$Fe(CO)_2(NO)_2$[b]	$Co(CO)_3NO$[c]	$Ni(CO)_4$[d]
r(CO)		1.145 (6)	1.140 (4)	1.140 (5)	1.141 (2)
r(NO)	1.171 (2)	1.167 (2)	1.171 (4)	1.167 (16)	
r(MC)		1.949 (7)	1.883 (3)	1.842 (3)	1.838 (2)
r(MN)	1.763 (2)	1.717 (2)	1.688 (3)	1.671 (5)	
∠CMC			110.2 (25)	110.2 (22)	[109.5]
∠CMN		106.2 (49)	108.4 (13)	108.7 (23)	
∠NMN	[109.5]	112.5 (43)	114.2 (62)		
n(MC)[e]		1.26	1.51	1.67	1.65
n(MN)	1.89	2.13	2.26	2.42	
$\sum n$[f]	7.56	7.65	7.54	7.43	6.60

[a] Distances (r_g) are in angstroms, and angles ($\angle_\alpha$) are in degrees. Parenthesized values are 2σ estimates. Quantities in square brackets were assumed. [b] This work. [c] Reference 7, model A. [d] Reference 3a. [e] For calculation of bond orders see text. [f] $\sum n = in(MC) + (4 - i)n(MN)$.

Discussion

Although no tests were made to assess a possible nonlinearity of the M–Y–O groups, the excellent agreement agreement between observed intensities and those calculated with the assumption of group linearity precludes any appreciable deviation from it. This conclusion is consistent with the result obtained in the case of $Co(CO)_3NO$[7] where the Co–N–O bond angle was investigated and found to be indistinguishably different from 180°. Taken together, the evidence from investigations of the four molecules strongly supports the view that M–N–O groups in d^{10} tetrahedrally coordinated complexes are linear, or very nearly so.

The qualitative molecular orbital picture of the bonding between transition metals and carbonyl or nitrosyl groups has the bonds composed of a σ component obtained by donation of an unshared pair from the carbon or nitrogen atom to the metal and a π component obtained by back-donation of $d\pi$ electrons from the metal to a π^* orbital on the ligand. If one imagines molecules in the isoelectronic series $M(CO)_n(NO)_{4-n}$ (M = Cr, Mn, Fe, Co, Ni) to be generated from $Cr(NO)_4$ by successive transfer of a proton from a nitrogen atom to the metal, the additional $d\pi$–π^* back-bonding that follows prevents buildup of formal charges. To the extent that *any* $d\pi$–π^* back-bonding to a particular ligand exists, one expects to find the M–C or M–N bond to be shorter than a nominal single bond and the corresponding intraligand bond to be longer than that in carbon monoxide (r_g = 1.133 Å) or nitric oxide (r_g = 1.156 Å). Structural results for the five compounds are summarized in Table VII. The C–O and N–O bonds are in every case longer than those in carbon monoxide and nitric oxide, and as we show below, both the M–C and M–N bonds are considerably shorter than the sums of the covalent single-bond radii. The evidence for extensive back-bonding is thus conclusive.

In order to determine the relative amounts of back-bonding in each of the five compounds of Table VII, we investigated the differences in the lengths of corresponding bond types. The molecule-to-molecule differences in the C–O and N–O bond lengths are too small to be detected, but those for the M–C and M–N bonds are both substantial and precisely determined. Since the amount of back-bonding is clearly connected with bond multiplicity, we calculated the bond orders of these bonds with use of Pauling's empirical equation[18] $D(1) - D(n) = 0.71 \log n$. There is uncertainty about the lengths of the single bonds ($D(1)$) to be used for our molecules, but tests showed that although the bond order values (n) depend on the choice, neither the changes in bond order nor the intramolecular differences $n(M\text{–}N) - n(M\text{–}C)$ are very sensitive to it. We arbitrarily adopted Pauling's ennea radii[19] for the metal atoms (these decrease in steps of 0.01 Å from Cr at 1.26 Å to Ni at 1.22 Å) and his values of 0.77 and 0.70 Å for the C and N radii to the metals to generate the $D(1)$ values. It is found (Table VII) that there is a clear tendency for the bond orders of both the M–C and M–N bonds to increase as the atomic number of the metal increases except for $Ni(CO)_4$, where the M–C bond order is about the same as in $Co(CO)_3NO$. With the assumption that bond orders greater than unity reflect back-bonding, there is seen to exist a substantial amount of back-bonding in each of the M–N links that increases steadily throughout the series and a lesser amount in the M–C links that also increases through $Co(CO)_3NO$. These results might at first be thought to imply a stepwise increase in the total amount of metal-to-ligand bonding from the chromium to the cobalt compound, but the sums of the bond orders of the metal bonds are nearly constant. If, as these bond order sums suggest, the number of bonds ($\sigma + \pi$) formed by the metal atoms of the series does not change much, the bond order changes must be due to redistribution of the π components as the ligands change. The bond order values of Table VII suggest the following interpretations. The shift of a proton from a nitrogen atom to the metal in $Cr(NO)_4$ to form the manganese compound leads to an Mn–C bond that is much weaker than both the M–N one it replaced and those with which it coexists. The small value for the Mn–C bond order

---

(18) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Chapter 7.

(19) Pauling, L. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 746.

Inorg. Chem. **1985**, *24*, 2771-2774

indicates that the dπ bonding from the replaced ligand has been nearly entirely shifted to the remaining nitrosyls, strengthening the Mn–N bonds relative to the Cr–N bonds. Formation of the iron compound from the manganese compound, and subsequently the cobalt from the iron, by the same mechanism has similar consequences. In these cases, however, the competitive advantage of nitrosyls over carbonyls has been reduced first from 3:1 to 2:2, and then to 1:3, which results in a more equitable distribution of the "excess" dπ bonding and leads to increases in the bond orders of both types of ligands.

It is notable that in the isoelectronic series under discussion the M–N bond orders are substantially greater than the M–C bond orders for the three molecules in which they coexist and the Cr–N bond order is substantially greater than the Ni–C bond order. These facts leave no doubt that a nitrosyl group is a much better π-electron acceptor than is a carbonyl group. Jolly and coworkers[2,20] have discussed the back-bonding to, and π-acceptor properties of, nitrosyl and carbonyl ligands on the basis of studies of carbon, nitrogen, and oxygen core binding energies from XPS experiments and ligand-stretching force constants. Among their conclusions are that the NO groups are much better π acceptors than CO, that the back-bonding to the CO groups diminishes only slightly from $Ni(CO)_4$ to $Fe(CO_2(NO)_2$ and then much more in the step to $MnCO(NO)_3$, and that the total amount of back-bonding increases from $Ni(CO)_4$ to $Cr(NO)_4$ in the series. These conclusions are completely consistent with ours. However, their data are also reported to be consistent with increasing back-bonding to the NO groups as the atomic number of the metal decreases whereas ours clearly are not.

Finally, it should be emphasized that it is the relative values of the M–N and M–C bond orders in Table VII and their trends from compound to compound that have significance, not the values themselves. The latter are very sensitive functions of the radii used to calculate them and hence are unreliable. The values given in the table seem reasonable, however, because they are consistent with the principle that the charges on the central atoms not be greater than unity. For example, a bond order sum of 7.5 corresponds to a formal charge of 0.5– on the metal atom, which is reduced by electron flow to the ligands impelled by the metal–ligand electronegativity difference. In the case of $Cr(NO)_4$ an assumed electronegativity difference of 1.4 corresponds to about 38% ionic character for the Cr–N bonds and hence to a net charge of about 1.0+ on chromium. A similar calculation for $Ni(CO)_4$ (with a bond order sum of 6.5) leads to a residual charge of about 1.0– on nickel. Values for the other compounds lie between these.

Acknowledgment. This work was supported by National Science Foundation Grants CHE78-04258 and CHE81-10541 to Oregon State University and by a grant to the University of Texas from the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. $Cr(NO)_4$, 37355-72-9; $Mn(CO)(NO)_3$, 14951-98-5; $Fe(CO)_2(NO)_2$, 13682-74-1.

Supplementary Material Available: Tables of the force field and symmetry coordinates for $Fe(CO)_2(NO)_2$ and the total scattered intensities, calculated backgrounds, and averaged molecular intensities for each substance (23 pages). Ordering information is given on any current masthead page.

---

[20] Avanzino, S. C.; Bakke, A. A.; Chen, H.-W.; Donahue, C. J.; Jolly, W. L.; Lee, T. H.; Ricco, A. J. *Inorg. Chem.* **1980**, *19*, 1931.

Contribution from the Department of Chemistry,
Oregon State University, Corvallis, Oregon 91331

Structure and Bonding in Transition-Metal Carbonyls and Nitrosyls. 2. Gas-Phase Electron Diffraction Reinvestigation of Tricarbonylnitrosylcobalt

KENNETH HEDBERG,* LISE HEDBERG, KOLBJØRN HAGEN, ROBERT R. RYAN,[1] and LLEWELLYN H. JONES[1]

Received October 26, 1984

The structure of gaseous $Co(CO)_3NO$ has been studied at room temperature. As with the data for the other $M(CO)_n(NO)_{4-n}$ compounds of the first transition group,[16] the data are completely consistent with linear MYO groups although small deviations from linearity cannot be ruled out. Values of the bond distances (r_g) and bond angles ($\angle_\alpha$) based on C_{3v} symmetry, with estimated 2σ uncertainties, are $r(\text{Co—N}) = 1.671$ (6) Å, $r(\text{Co—C}) = 1.843$ (3) Å, $r(\text{N=O}) = 1.180$ (14) Å, $r(\text{C=O}) = 1.136$ (4) Å, $\angle\text{NCoC} = 107.7$ (14)°, and $\angle\text{CCoC} = 111.2$ (13)°; the values reflect corrections for the effects of vibrational averaging (shrinkage) and anharmonicity.

Introduction

Transition-metal complexes with nitric oxide ligands (nitrosyl complexes) have structures in which the MNO groups tend to be either nearly linear or rather strongly bent. On the chemical side, these structures have been respectively interpreted as the consequence of a reaction wherein the ligand has acted as a base (NO^+) or an acid (NO^-) according to the character of the metal center. More recently, theoretical considerations have provided an understanding of the structure of the MNO groups in terms of molecular orbital models that depend on the coordination and number of d electrons of the metal, with suitable perturbations related to the σ and π type interactions of the other ligands. Several discussions of bonding models[2-6] as well as excellent review articles[6-8] of the chemical and structural literature in this area are available.

Tricarbonylnitrosylcobalt ($Co(CO)_3NO$) is a d^{10} or $\{MNO\}^{10}$ complex; the latter symbolism, suggested by Enemark and Feltham,[6] designates the number of 3d electrons in the metal plus one from the π^* orbital of each NO ligand. According to theory for such tetrahedrally coordinated complexes, the MNO groups will be linear or bent[2,3,6] depending on the relative energies of the $4a_1$ (z^2, σ(NO)) and 4e (xz, yz, π^*(NO)) orbitals—energies that are more difficult to predict than for systems in which the σ and π perturbations due to ancillary ligands are more clearly separated

---

[1] Present address: Los Alamos Scientific Laboratory, Los Alamos, NM 87545.

[2] Mingos, D. M. P. *Inorg. Chem.* **1973**, *12*, 1209.

[3] Hoffman, R.; Chen, M. M. L.; Elian, M.; Rossi, A. R.; Mingos, D. M. P. *Inorg. Chem.* **1974**, *13*, 2666.

[4] Fenske, R. F.; Jensen, J. R. *J. Chem. Phys.* **1979**, *71*, 3374.

[5] Bursten, B. E.; Jensen, J. R.; Gordon, D. J.; Treichel, P. M.; Fenske, R. F. *J. Am. Chem. Soc.* **1981**, *103*, 5226.

[6] See: Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339 and references cited therein.

[7] Caulton, K. G. *Coord. Chem. Rev.* **1975**, *14*, 317.

[8] Feltham, R. D.; Enemark, J. H. *Top. Stereochem.* **1981**, *12*, 155.

0020-1669/85/1324-2771$01.50/0