The exo orientation of the NO group in C_4F_7NO, i.e. eclipsed position with respect to F_1, corresponds to the eclipsed conformation observed for CF_3NO. No gas-phase structural data are known for a nitroso or isoelectronic carboxaldehyde group bonded to cyclobutane, which would allow comparison of the position of such groups relative to the ring. In nitrosocyclopropane the preference for the exo orientation of the NO group has been determined by microwave spectroscopy and no transitions corresponding to any other orientation were observed.[14] For cyclopropanecarboxaldehyde both conformers, exo and endo, are nearly equally favored[15] and this result is in agreement with theoretical considerations.[16]

The nitroso group causes considerable angle distortion of the cyclobutane ring ($C_2C_1C_4 = 91.4$ (6)° vs. $C_1C_2C_3 = 86.3$ (6)°), resulting in a shorter $C_1 \cdots C_3$ distance (2.15 Å) than $C_2 \cdots C_4$ distance (2.25 Å).

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Theoretical Investigation of the Molecular Structure of Manganese Dichloride

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The present theoretical investigation is an extension of previous experimental electron diffraction studies of the molecular structure of first-row transition-metal dihalides: $MnCl_2$,[2] $MnBr_2$,[3] $FeCl_2$,[4] $FeBr_2$,[4] $CoCl_2$,[5] $CoBr_2$,[6] and $NiBr_2$.[7] These studies have pointed to a linear configuration for these molecules while exhibiting large-amplitude, low-frequency bending vibrations. Current electron diffraction analyses of the molecular structure of vanadium dichloride[8] and chromium dichloride,[8] however, indicate that these molecules may have a highly bent structure with bond angles in the vicinity of 110°. These analyses are in progress and are indeed complicated by the presence of different amounts of dimeric species. Such mixtures have been successfully analyzed for manganese dibromide[3] and iron dibromide[4] as well as for cobalt dibromide.[6] The emerging bent monomeric structures for VCl_2 and $CrCl_2$, however, prompted us to initiate a theoretical investigation on the geometry and electronic structure of the ground-state dichloride monomeric species. As a benchmark for further

calculations on other transition-metal dichlorides, the manganese dichloride molecule was chosen. The choice of $MnCl_2$ was motivated both by the relative ease of computation for the d^5 configuration and by the good experimental electron diffraction data available for this molecule.[2] Our calculations were essentially completed when a recent matrix-isolation infrared spectroscopic study[9] came to our attention, reporting a bent structure for the dichlorides of iron, cobalt, and nickel, with a bond angle of about 160°. The electron diffraction data on all these molecules have been interpreted with a linear equilibrium configuration; $FeCl_2$ and $CoCl_2$ have been studied in our Budapest laboratory,[4,5] and the structure of $NiCl_2$ has been determined in Professor Hedberg's laboratory.[10] The apparent controversy has already been commented upon.[11] A reanalysis of the electron scattering data of iron dichloride and additional spectroscopic calculations[11] reinforce the linear structure for this molecule. Calculations on magnanese dichloride are instructive also in this respect since the electron diffraction analyses led to analogous results for the whole series of $MnCl_2$, $FeCl_2$, $CoCl_2$, and $NiCl_2$ molecules.

The low-frequency, large-amplitude bending vibrations and the high-temperature experimental conditions make the electron diffraction analysis of a molecule like manganese dichloride less straightforward than those of more rigid molecules. For this reason the experimental results[2] will be briefly summarized. The nozzle temperature of the manganese dichloride experiment was approximately 800 °C. The thermally averaged internuclear distances[12] were determined to be r_g(Mn–Cl) = 2.205 ± 0.005 Å and r_g(Cl$\cdots$Cl) = 4.324 ± 0.015 Å. If the equilibrium confirguration is assumed to be linear, the $2r_g$(Mn–Cl) − r_g(Cl$\cdots$Cl) difference is the linear shrinkage, $\delta_g = 0.086$ Å. This shrinkage is the consequence of large-amplitude bending vibrations, and under this assumption it was used to estimate the bending vibrational frequency, $\nu_2 = 93 \pm 8$ cm^{-1}. This estimated frequency compared well with the value 83 cm^{-1} reached from a matrix-isolation infrared spectroscopic investigation.[13] This rather good agreement, in fact, supported the assumption for the linear equilibrium configuration. Originally this assumption was based on the lack of the symmetric stretching frequency in the infrared spectrum[13] and the absence of a permanent electric dipole moment as concluded from the molecular beam deflection experiments.[14]

Although all experimental evidence is consistent with a linear equilibrium geometry, the experimental data refer directly to an average structure resulting from averaging over all intramolecular motion. On the other hand, the theoretical calculations refer directly to the equilibrium configurations. As the manganese dichloride study was considered to be a bench mark one for further calculations on other transition-metal dihalides, it was also decided to examine the applicability of various levels of basis set sophistication to determine a reasonable level of theory for use in future work.

Computational Details

All ab initio calculations were carried out with the GAMESS series of programs.[15] The structural parameters that were varied in the calculations are the Mn–Cl bond distance and the Cl–Mn–Cl bond angle. Restricted open-shell calculations for the open-shell sextet states were carried out by using Davidson's method.[16] The open shell calculations were performed on the $...1\delta_g^2 3\pi_g^2 g\sigma_g^1$ configuration for linear $D_{\infty h}$ geometry and $...3a_2^1 10b_2^1 13a_1^1 5b_1^1 14a_1^1$ configuration for bent C_{2v} geometries.

Several different basis sets were employed for the present calculations on $MnCl_2$. Basis I consists of the STO-3G basis of Hehre et al.,[17] which

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Table I. Parameters Used in the EH and INDO Calculations

	H_{ii}, eV	exponents	
orbital	EH	EH	INDO
Mn, 4s	−8.46	1.800	1.650
Mn, 4p	−4.92	1.800	1.650
Mn, 3d	11.31	5.150 (0.5320)	5.7574 (0.3898)
		1.90 (0.6490)	2.5097 (0.7297)[a]
Cl, 3s	−25.71	2.130	2.130
Cl, 3p	−13.60	2.130	2.130

[a] Reference 19.

Table II. Bond Distances and Total Energies for $MnCl_2$ Calculated with Different Basis Sets

Mn basis[a]	type	Mn–Cl dist, Å	E_{Total}, au
I	STO-3G	2.149	−2047.163 71
II	STO-3G(2d)	2.208	−2048.753 65
III	Hay (10s 7p 3d)	2.289	−2068.928 74
	Hay (10s 7p 3d)[b]	2.267	−2068.945 49
IV	Goddard (10s 7p 3d)	2.294	−2068.929 37
		2.205 (5)[c]	

[a] See text for a description of basis sets. [b] d-Polarization function (0.6) added to Cl basis. [c] Experimental bond distance, r_g (see text).

contains a single-ζ exponent for the 3d function.[18] Since it is well known that the 3d orbital cannot be adequately represented by a single exponent, basis II employed an STO-3G basis for each of the two Slater orbitals optimized for the Mn atom by Clementi et al.[19] This had the effect of allowing the 3d orbitals of Mn to have a double-ζ contraction, and it was named STO-3G(2d). Basis III for Mn involves the Wachters (14s 9p 5d)[20] set extended to 6d as recommended by Hay[21] with one additional p function to describe the 4p orbital as discussed by Schaefer[22] to give Mn (14s 10p 6d/10s 7p 3d). The final basis (basis IV) is similar to basis III except that the 6d basis of Hay is replaced by the 6d basis of Goddard.[23]

The STO-3G basis for Cl[24] was used with the small basis sets (I and II) of Mn. To match the larger basis sets for the Mn atom (III and IV), the chlorine basis consisted of (11s 7p/6s 4p) taken from Dunning and Hay,[25] to which a d polarization function ($\alpha = 0.06$) was also added.

Semiempirical calculations of the extended-Hückel (EH) type were carried out with the program FORTICON8,[26] while INDO calculations were performed with a recent version of Zerner's program.[27] In these calculations only bond angles were varied, and the Mn–Cl distance was kept fixed at the experimental value.[2] Both the EH and INDO calculations employed double-ζ functions for the d orbitals. The parameters used in the EH and INDO calculations are summarized in Table I.

Geometry optimizations for the ab initio calculations utilized a gradient method in which the gradient was reduced to less than 2.0 millihartrees/bohr.

For the optimizations employing small Mn basis sets (I and II) C_{2v} symmetry was used to determine the possibility of obtaining a bent $MnCl_2$ structure. The optimized geometries obtained with larger basis sets for Mn (III and IV) utilized D_{4h} symmetry, a subgroup of the higher order $D_{\infty h}$ symmetry for linear $MnCl_2$.

Results and Discussion

The total energies and Mn–Cl bond distances for $MnCl_2$ from several different basis sets are given in Table II. The experimental Mn–Cl bond distance is 2.205 (5) Å, and the best agreement with the calculated values comes from the STO-3G(2d) basis. Since the experimental value for the Mn–Cl bond distance is derived
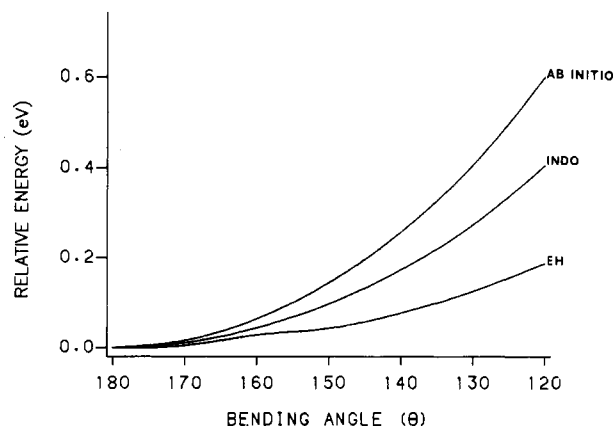

Figure 1. Energy of $MnCl_2$ as a function of the bending angle (θ) for different calculational methods. The energies are relative to the linear geometry, and the experimental Mn–Cl bond distance was used.
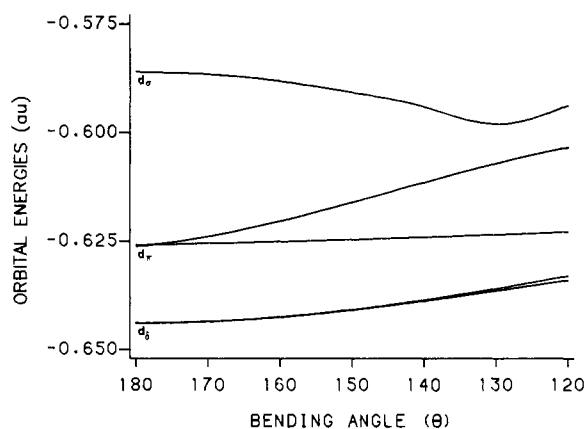

Figure 2. Orbital energies of $MnCl_2$ as a function of the Cl–Mn–Cl bending angle for ab initio calculations employing the STO-3G(2d) basis for Mn.

from electron diffraction data, which is known to incorporate vibrationally averaged Mn-Cl distances, the equilibrium Mn–Cl distance may actually be less than 2.205 Å. Thus the STO-3G results appear to give good agreement with experiment and are probably fortuitous. Interestingly, the large basis set calculations in Table II yield much larger Mn–Cl distances than the small basis sets. The addition of a d polarization function on the Cl atom provides some decrease in the Mn–Cl distance but not enough to provide adequate agreement with the experimental value. The trend of ab initio calculations yielding transition-metal–ligand distances larger than experimental values is similar to that obtained previously for ferrocene.[28] Moreover, unlike molecules derived from first-row atoms, where the use of better basis sets and consideration of electron correlations leads to larger bond lengths, the opposite may be true for molecules containing transition-metal atoms. These molecules may contain many unfilled molecular orbitals that are bonding between the metal and the ligand. Calculations including electron correlation in which electrons are excited to these molecular orbitals would tend to shorten bonds.[29]

Figures 1 and 2 reveal interesting results. In Figure 1, the total energy as a function of the Cl–Mn–Cl bending angle (θ) is given for ab initio STO-3G(2d) calculations as well as the INDO and extended-Hückel (EH) semiempirical calculations. All calculational methods agree with experiment in producing a linear geometry. The most interesting and far-reaching results for future work on other metal chlorides is revealed by the Walsh[30] diagram

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given in Figure 2, where energies of the orbitals of MnCl$_2$ with substantial d character are plotted against the bending angle (θ). The d$_\delta$ orbitals are degenerate at 180° but split and gently rise in energy for smaller values of θ. The d$_\pi$ orbitals are also energetically degenerate at 180°, but one d$_\pi$ component rises in energy rapidly for small values of θ while the other d$_\pi$ component undergoes a gradual ascent. In contrast, the d$_\sigma$ orbital decreases in energy as θ decreases.

The behavior of the d orbitals in Figure 2 as a function of θ can be contrasted with similar curves for previous calculations on ZnF$_2$[31] and MnH$_2$.[32] For both ZnF$_2$ and MnCl$_2$ the F(2p$_\pi$) and Cl(3p$_\pi$) orbitals are antibonding with respect to the metal d$_\pi$ orbitals. Thus, as θ decreases, the d$_\pi$ component that rises rapidly on bending is the result of the loss of a metal(3d$_\pi$)–ligand(p$_\pi$) antibonding interaction coupled to an increasing ligand (σ) antibonding interaction, with the latter prevailing. These two effects lead to the destabilization of the d$_\pi$ orbitals in both MnCl$_2$ and ZnF$_2$. For MnCl$_2$ the d$_\sigma$ orbital energy *decreases* on bending but *increases* on bending for ZnF$_2$. This behavior can be attributed to both a larger antibonding interaction with the d$_{z^2}$ orbital in ZnF$_2$ than in MnCl$_2$ and a stronger Mn(d$_{z^2}$) + λ4s mixing, which would favor bending. The situation for MnH$_2$ produces a Walsh diagram similar to that for MnCl$_2$, but the absence of π orbitals on H produces some differences.

It is possible to derive a qualitative model from Figure 2 to give useful information about the trends in geometry and electronic structure of other transition-metal dichlorides. A d^4 CrCl$_2$ molecule with electronic configuration ...$1\delta_g{}^2 3\pi_g{}^2$ would most likely be linear.[33] Interestingly, experimental studies of high-temperature CrCl$_2$ and VCl$_2$ vapors[8] appear to point to bent structures for these molecules. This can be reationalized on the basis of Figure 2, supposing that the electronic configuration of CrCl$_2$ would not be ...$1\delta_g{}^2 3\pi_g{}^2$ but rather ...$1\delta_g{}^2 3\pi_g{}^1 9\sigma_g{}^1$. In this case an electron is removed from the d$_{yz}$ orbital, which rises rapidly in energy on bending, and is placed in a d$_{z^2}$ orbital, which decreases in energy upon bending. Thus the CrCl$_2$ molecule would favor a bent geometry with a lower total energy than for the linear configuration. The same reasoning is applicable to the d^3 VCl$_2$ molecule. In future work, we propose to investigate our model further and to determine the electronic structure of other transition-metal dichlorides.

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Chemical Oxidation of Binuclear Rhodium(I) Complexes with Silver Salts. Synthesis and X-ray Crystal Structure of the Paramagnetic Rh$_2{}^{5+}$ Formamidinate Complex Rh$_2$(Form)$_3$(NO$_3$)$_2$

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The chemistry of the complexes characterized by the presence of Rh$_2{}^{4+}$ core is still an attractive field of research, and a wealth of experimental data, complemented by theoretical studies, are available for such complexes.[1] In contrast, little is known on complexes containing the Rh$_2{}^{5+}$ core mainly because these species have been rarely isolated.[2,3] These complexes in fact are generated when the Rh$_2{}^{4+}$ derivatives Rh$_2$(carboxylate)$_4$ are electrochemically oxidized, undergoing a one-electron oxidation at a potential that is dependent on the electronic properties of the bridging ligands.[1] Recently Bear and co-workers synthesized the series of mixed-ligand Rh$_2{}^{4+}$ complexes[4] Rh$_2$(ac)$_n$(acam)$_{4-n}$ (ac = [O$_2$CCH$_3$]$^-$, acam = [HNOCCH$_3$]$^-$, n = 0–4) showing that the redox potential for the Rh(II,II) $\rightleftharpoons$ Rh(II,III) conversion is a function of the number of the acetamidate groups. On the other hand, it is known that the electrochemical oxidation of the trifluoroacetate derivative Rh$_2$(O$_2$CCF$_3$)$_4$ does not occur up to 1.8 V vs. SCE.[5] The existence of species containing the Rh$_2{}^{4+}$ or Rh$_2{}^{5+}$ cores is then determined from the donor properties of the bridging ligands. So a careful adjustment of the electronic density on the rhodium atoms by means of the appropriate ligands could permit the synthesis of complexes containing the Rh$_2{}^{4+}$ or Rh$_2{}^{5+}$ cores.

We have found a synthetic route that enabled us to synthesize the mixed-ligand complex Rh$_2$(Form)$_2$(O$_2$CCF$_3$)$_2$(H$_2$O)$_2$ (Form = [p-MeC$_6$H$_4$NC(H)NC$_6$H$_4$Me-p]$^-$) containing the Rh$_2{}^{4+}$ core[6] and the mixed-valence complex Rh$_2$(Form)$_3$(NO$_3$)$_2$ containing the Rh$_2{}^{5+}$ core. This method is based on the chemical oxidation with the appropriate silver salt of the Rh(I) formamidinate complex [Rh(C$_8$H$_{12}$)(Form)]$_2$. In this paper we describe the synthesis, the spectroscopic properties, and the X-ray crystal structure of the complex Rh$_2$(Form)$_3$(NO$_3$)$_2$.

Experimental Section

Preparation of Rh$_2$(Form)$_3$(NO$_3$)$_2$. [Rh(C$_8$H$_{12}$)(Form)]$_2$[7] (0.400 g, 0.46 mmol) was dissolved in 100 mL of a CH$_2$Cl$_2$–CH$_3$OH (1:1) mixture, and silver nitrate (0.156 g, 0.92 mmol) dissolved in water (1 mL) was added in the dark. The solution suddenly turned green while a gray precipitate of silver metal was formed. The mixture was stirred at room temperature for $\simeq$4 h to effect reaction, indicated by the final blue-violet color. The solution was then filtered on a short Celite column to remove the silver, and the solvent was evaporated under reduced pressure until crystallization commenced. The deposition was completed by allowing the solution to stand overnight. The black-violet solid obtained was collected and crystallized from benzene–heptane, affording 0.250 g of complex (yield 63%). Anal. Calcd for C$_{45}$H$_{45}$N$_8$O$_6$Rh$_2$: C, 54.06; H, 4.53; N, 11.20; O, 9.60. Found: C, 54.23; H, 4.50; N, 10.91; O, 9.61.

X-ray Data Collection and Structure Refinement. Suitable black-violet crystals of the complex of cubic habit were obtained by slow evaporation from a benzene–heptane solution. A crystal of approximate dimensions 0.10 × 0.10 × 0.09 nm was selected and mounted on a Siemens-Stoe automatic four-circle diffractometer. Accurate unit-cell dimensions and crystal orientation matrices together with their estimated standard errors were obtained from least-squares refinement of the 2θ, ω, χ, and ϕ values of 25 carefully centered high-angle reflections using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). The complex crystallizes in the triclinic space group P$\bar{1}$, with a = 11.791 (1) Å, b = 13.066 (2) Å, c = 16.881 (4) Å, α = 110.69 (3)°, β = 92.89 (2)°, γ = 114.68 (3)°, V = 2149.96 Å^3, $F(000)$ = 1018, Z = 2, and D_{calcd} = 1.664 g cm^{-3}. X-ray data were collected at room temperature for all independent reflections in the range 3 ≤ 2θ ≤ 50°. An ω–θ scan technique was used for each reflection with a scan speed 0.03° s^{-1} and scan width 1.2°. No reflections were sufficiently intense to require the insertion of attenuators into the beam. Three standard reflections were monitored periodically during the

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