compensates for the repulsive interactions between the sulfur atoms by increasing the S–C–C′–S′ torsion angle. An increase in this angle effects an increase in the intersulfur distances and also directs the sulfur lone pairs slightly away from the molecule's 3-fold rotation axis. For complexed TTCN the stabilization provided by formation of the metal–sulfur bonds partly overcomes the repulsion between the sulfur atoms. Thus the S–C–C′–S′ torsion angle is smaller, and the intersulfur distance is shorter for the complexed molecule as compared to uncomplexed TTCN. Because the sulfur σ-donor orbitals of complexed TTCN are directed slightly away from the 3-fold axis, a trigonal distortion is observed in the (TTCN)Mo(CO)$_3$ molecule, which is the result of an optimization of the orbital overlap of the thioether σ-donor orbitals with the empty metal acceptor orbitals (**2a**). The S–C–C′–S′ torsion angle also governs the intersulfur distances in (TTN)Mo(CO)$_3$. However, the open chain of TTN leads to S1–C5–C6–S2 and S2–C7–C8–S3 torsion angles, which are of equal magnitude but opposing sign. This stereochemistry permits each σ-donor orbital on sulfur to point directly at the metal atom (**2b**).[17] It is interesting that the magnitudes of the S–C–C′–S′ torsion angles in (TTCN)Mo(CO)$_3$ and (TTN)Mo(CO)$_3$ are similar. As a result, the S1··S2 and S3··S2 interatomic distances in (TTN)Mo(CO)$_3$ are comparable to the average intersulfur distance in (TTCN)Mo(CO)$_3$. However, the S1··S3 interatomic distance in (TTN)Mo(CO)$_3$ is significantly longer. This is likely the result of a repulsive filled–filled interaction between the π-donor orbitals on S1 and S3.[2,18] Finally, the S1–C5–C6–S2 and S2–C7–C8–S3 torsion angles could, in principle, change signs (e.g. S1–C5–C6–S2 = −46.0° and S2–C7–C8–S3 = 48.3°) without affecting the intersulfur distances; however, this torsional change rotates the thioether π-donor orbitals on S1 and S3 toward one another and consequently should be sterically disfavored.

For (TTN)Mo(CO)$_3$, the average Mo distance to S1 and S3 (2.578 (4) Å) is longer than the distance to the central sulfur atom (Mo–S2 = 2.528 (1) Å), which is similar to the average Mo–S distance in (TTCN)Mo(CO)$_3$ (2.52 (2) Å). The longer Mo–S1 and Mo–S3 distances as compared to the Mo–S2 distance in (TTN)Mo(CO)$_3$ may be another consequence of the repulsive filled–filled interaction between S1 and S3 in coordinated TTN (vide supra).

If the thioether σ-donor orbitals in (TTN)Mo(CO)$_3$ are indeed more favorably directed toward the empty metal orbitals than for (TTCN)Mo(CO)$_3$, then TTN should be a better electron donor than TTCN. The slightly lower carbonyl stretching frequencies for (TTN)Mo(CO)$_3$ (ν_{CO}(nitromethane) = 1927, 1815 cm^{-1}) than for (TTCN)Mo(CO)$_3$ (ν_{CO}(nitromethane) = 1935, 1825 cm^{-1}) seem to support this.

Acknowledgment. The crystal structure of (TTN)Mo(CO)$_3$ was solved at the University of Arizona Molecular Structure Laboratory. Financial support of this work by NIH Grant ES 00966 (J.H.E.) and Department of Energy Contract DE-AC0280ER10746 (D.L.L.) is gratefully acknowledged. We also thank Dr. C. G. Young for obtaining the ^{95}Mo NMR spectrum of (TTN)Mo(CO)$_3$.

Registry No. (TTN)Mo(CO)$_3$, 102941-85-5; TTN, 37460-04-1; bis(2-mercaptoethyl) sulfide, 3570-55-6.

Supplementary Material Available: Figure 3, showing a stereoscopic ORTEP drawing of the unit cell, Table VII, listing the anisotropic thermal parameters for the non-hydrogen atoms, and Table VIII, listing the refined positions of the hydrogen atoms (3 pages). Ordering information is given on any current masthead page.

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^{1}H and ^{13}C NMR Spectra of a Series of Methyl-Substituted Imidazole Complexes of Pentaamminecobalt(III) and Crystal Structure of the Remote Isomer of [(4-Methylimidazole)pentaamminecobalt(III)] Trichloride Dihydrate

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Received November 22, 1985

The crystal structure for the remote isomer of [(4-methylimidazole)pentaamminecobalt(III)] trichloride dihydrate, CoC$_4$H$_{21}$N$_7$Cl$_3$·2H$_2$O, was determined from 1775 reflections (Mo Kα) to $R = 0.04$ ($R_w = 0.043$); the space group is $Pna2_1$. The unit cell constants a, b, and c are 7.011 (2), 10.373 (3), and 21.420 (3) Å; $\alpha = \beta = \gamma = 90.0$ (0)° (orthorhombic). The number of molecules per unit cell, Z, is 4. Coordination of the 4-methylimidazole ligand occurs via the 5-methylimidazole tautomer, e.g., the remote isomer. The Co–cis-NH$_3$ bond lengths average 1.96 Å, ranging between 1.930 (6) and 1.992 (10) Å; the Co–trans-NH$_3$ band exhibits no discernible trans effect at 1.976 (5) Å. The Co–N(3) (5-methylimidazole) distance is 1.945 (5) Å. The plane of the imidazole ring makes dihedral angles of 43.6 and 41.9° with the Co–cis-NH$_3$ planes. ^{1}H and ^{13}C NMR data for the free ligands and their Co(NH$_3$)$_5$$^{3+}$ complexes are reported for the following L: 1-methylimidazole; 2-methylimidazole; 4-methylimidazole; 5-methylimidazole; 1,2-dimethylimidazole; 1,4-dimethylimidazole; 1,5-dimethylimidazole; 2,5-dimethylimidazole. Ring carbons in the C(2) and C(5) positions show downfield ^{13}C shifts ($\Delta\delta_C$) upon coordination while C(4) carbons exhibit upfield shifts or smaller downfield shifts than C(2) or C(5). Methyl ring substituents follow the shift of their ring carbon or are shifted downfield for N-methylation. The ^{1}H shifts relative to those of the free ligands ($\Delta\delta_H$) show downfield shifts at all ring positions, but the H(4) proton undergoes smaller downfield shifts. The origin of the shifts upon coordination ($\Delta\delta_H$ and $\Delta\delta_C$) are explained on the basis of an induced rehybridization of the ring carbons upon coordination of a withdrawing metal center at N(3) of the imidazole ring.

Introduction

Nuclear magnetic resonance spectroscopy (NMR) has been used to evaluate the changes in electron density within ligands upon coordination to a variety of metals. These electron density changes can occur by σ- and π-electron polarization, which are related to the σ basicity and the π-acceptor ability of the ligand. Complicating the interpretation of the NMR shift values are any of several local effects caused by anisotropy and electron currents within the metal fragments. These factors have been discussed for a range of ligands including organonitriles, pyridines, and diazines and their complexes Co(NH$_3$)$_5$L^{3+}, Ru(NH$_3$)$_5$L^{2+}, Rh(NH$_3$)$_5$L^{3+}, Fe(CN)$_5$L^{3-}, Co(CN)$_5$L^{2-}, and H$^+$.[1,2,9-13]

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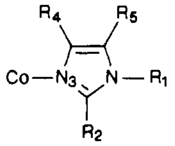
Recent work by Storm et al. has yielded ^1H NMR assignments and chemical shift values for pentaamminecobalt(III) complexes of substituted imidazoles.[8] This work made no attempt to explain the chemical shift differences vs. the free-ligand values. The cobalt system is of particular interest because the unimportance of π-back-bonding in cobalt(III) complexes and the lack of anisotropic effects of the ammonia spectator ligand set should simplify the interpretation of the $\Delta\delta$ values.

This paper discusses both the ^1H and ^{13}C NMR chemical shift changes in a series of pentaammine(substituted imidazole)cobalt(III) complexes with consideration of potential influences upon these changes. Ring methylation is used as a diagnostic aid, but there are two possible isomers for the complexes with L = 4-methylimidazole and L = 2,5-dimethylimidazole. The imidazole ring is numbered so that the pyrrole nitrogen is N(1) and the pyridine nitrogen is N(3)



The two isomers of the L = 4-methylimidazole complex have been previously separated,[4] and the X-ray structure contained in this paper establishes conclusively that the identity of the more stable isomer is the remote 5-methylimidazole complex.

Experimental Section

Preparations. The cobalt complexes were prepared from aquopentaamminecobalt(III) perchlorate by minor variations of literature methods.[1-3] The two isomers of the complex prepared with L = 4-methylimidazole were separated by fractional crystallization according to the method of Hoq et al.[4] The 1,4-dimethylimidazole and 1,5-dimethylimidazole ligands were synthesized by N-methylation of 4-methylimidazole and separation by chromatography on an alumina column.[5] The 2,4-dimethylimidazole (Gallard Schlesinger) and imidazole, 2-methylimidazole, 4-methylimidazole, 1-methylimidazole, and 1,2-dimethylimidazole (Aldrich) ligands were used without further purification. The complexes were isolated as orange microcrystalline solids that exhibited the proper UV–vis and IR spectra.

^1H and ^{13}C NMR Spectra. NMR data were obtained with a Bruker WH-300 spectrometer operating at 75.45 and 300.0 MHz for the ^{13}C and ^1H NMR studies, respectively. Ligand and complex ^1H NMR results were taken in dimethyl-d_6 sulfoxide solutions with tetramethylsilane (Me_4Si) as the internal reference. The ^{13}C NMR spectra were measured in 50% H_2O/50% D_2O solutions with *p*-dioxane as the internal reference. The ^{13}C NMR resonances are reported vs. external Me_4Si from the relationship $\delta_{ext}(Me_4Si) = \delta_{int}(diox) + 66.5$. Spectra of the complexes were obtained at concentrations near saturation and at ambient probe temperature.

X-ray Crystallography. A crystal of $[Co(NH_3)_5(4\text{-}MeIm)]Cl_3\cdot 2H_2O$ (Im = imidazole) having a size 0.175 × 0.175 × 0.625 mm was mounted on a Nicolet P3 four-circle X-ray diffractometer. The data were collected over the quadrant (000, *hkl*) by using a graphite-monochromated Mo Kα radiation source at room temperature. A total of 1775 reflections having $2.0° < \theta < 25.0°$ were measured with a θ–2θ scan; three standard reflections were measured every 50 reflections. Absorption corrections were calculated from a transmission curve based on azimuthal scans collected on the diffractometer using the program XEMP supplied by Nicolet. Cell parameters and systematic absences are consistent with the orthorhombic system, space group $P2_1cn$. The data were collected in this space group and transformed to the standard group $Pna2_1$.

Table I

formula	$CoC_4H_{21}N_7Cl_3\cdot 2H_2O$
fw	369
space group	orthorhombic $Pna2_1$
a, Å	7.011 (2)
b, Å	10.373 (3)
c, Å	21.420 (3)
α, deg	90.0 (0)
β, deg	90.0 (0)
γ, deg	90.0 (0)
vol, $Å^3$	1588.1 (5)
Z	4
calcd density, g cm^{-3}	1.54
abs coeff	16.3
F(000)	776
temp, °C	18
lattice measurement	
no. of reflcns	21
θ range	10–15
abs scan	
no. of reflcns	10
cor	0.317–0.351
data collcn	
θ range	2–25
h range	0–8
k range	0–12
l range	0–25
no. of decay stds	3
indices	
1	0,7,3
2	1,5,5
3	2,0,10
variation	0.983–1.008
reflcn count	
no. collcd	1775
no. rejected	11
no. unique	1527
no. unobsd	270
no. obsd	1257
σ level	2.5
R(merging)	0
refinement params	
final *R*	0.04
R_w	0.043
GOF	0.977
g	0.001
max Δ/σ	−0.914
max $\Delta(\rho)$	0.56
min $\Delta(\rho)$	−0.34

The position of Co was determined from Patterson methods. The positions of the remaining atoms were determined from subsequent difference Fourier syntheses. A least-squares refinement using anisotropic thermal parameters for all atoms and isotropic thermal parameters for the hydrogen atoms yielded $R = 0.04$ and $R_w = 0.043$ with a quality of fit of 0.977.

The refinement program minimized $\sum w(F_o - F_c)^2$ using $w = 1/(\sigma^2(F_o) + gF_o^2)$. The weights are based on counting statistics with instrumental instabilities accounted for by a constant factor in the final stages of the refinement. Scattering factors used were those taken from ref 16. Nicolet's R3m system of programs, which includes the programs SHELX, was used for analysis. The pertinent information concerning the acquisition of the diffraction data is given in Table I. Structure factor tables are available as supplementary material.

Results

^{13}C NMR Spectra. The ^{13}C NMR resonances for several methyl-substituted imidazoles and their complexes are tabulated in Table II. The free-ligand resonances were assigned by comparison with the values predicted by Koskinen[6] and agree with those values within 1–2 ppm, despite the difference in solvents used. The ring carbon resonances are estimated from Koskinen's relationship for 1,4-dimethylimidazole. In the coordinated species the carbons in positions 4 and 5 in the absence of methyl substitution at either position have been identified by decoupling experiments at low power. The ^1H resonances are assigned on the basis of literature protocols described.[8] Saturation of the downfield proton resonance (H(5)) in the $(NH_3)_5Co(1,2\text{-}Me_2Im)^{3+}$

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Table II. ^{13}C NMR Shifts (δ) of Substituted Imidazoles and Their $(NH_3)_5Co^{3+}$ Complexes

	C(2)	C(4)	C(5)	$CH_3(1)$	$CH_3(2)$	$CH_3(4)$	$CH_3(5)$
imidazole	136.0	121.9	121.9				
2-methylimidazole	145.7	121.4	121.4		12.54		
complex	149.0	127.4[c]	119.8[c]		12.91		
4-methylimidazole	135.1	132.2	117.8			10.57	
complex (A)	137.9	131.2	123.7			9.26	
5-methylimidazole[a]	135.1	117.8	132.2				10.57
complex (R)	138.8	118.1	137.5				11.84
1-methylimidazole	138.3	127.6	121.2	32.89			
complex	140.5	127.7[c]	125.0[c]	34.91			
1,2-dimethylimidazole	145.9	125.1	121.3	32.21	11.37		
complex	149.0	126.3[c]	124.8[c]	34.30	11.80		
1,4-dimethylimidazole	(136.4)	(138.5)	(116.5)	...		...	
complex	140.6	138.4	122.2	34.7		11.92	
1,5-dimethylimidazole	137.5	125.9	127.7	30.75			8.76
complex	139.9	124.4	133.2	32.36			8.29
2,5-dimethylimidazole[b]	144.7	116.7	131.8		12.53		10.71
complex	148.0	123.8	130.1		13.01		9.11

[a] Tautomer of 4-methylimidazole. [b] Tautomer of 2,4-dimethylimidazole. [c] Assignment based upon ^1H decoupling studies.

Table III. Correlation of ^{13}C $\Delta\delta$ Values by Carbon Type[a]

C(4)H	−6.0,[b] −0.3, −0.1,[b] −1.2,[b] +1.5, −7.1
*C(4)CH_3	+1.0, (+0.1)
C(4)*CH_3	+1.31
C(5)H	+1.6,[b] −5.9, −3.8,[b] −3.5,[b] (−5.7)
*C(5)CH_3	−5.3, −5.5, +1.7
C(5)*CH_3	−1.27, +0.47, +1.6
C(2)H	−2.8, −3.7, −2.2, (−4.2), −2.4
*C(2)CH_3	−3.3, −3.1, −3.3
C(2)*CH_3	−0.37, −0.43, −0.48
N(1)CH_3	−2.02, −2.09, −1.61

[a] Negative value denotes a downfield shift. Positive value denotes an upfield shift (relative to the free-ligand δ upon coordination). [b] Shifts determined by decoupling experiment.

complex causes the collapse of the upfield ^{13}C doublet. Saturation of the upfield proton (H(4)) causes collapse of the downfield ^{13}C doublet. This example is shown in Figure 1; results with the same interpretation were obtained for the 2-methylimidazole complex. With methyl substitution there is no ambiguity owing to ^{13}C–^1H coupling.

When complexation occurs, there are changes in the chemical shifts of the carbons in the ligands. These $\Delta\delta_C$ (=δ(free ligand) − δ(complex)) values have been calculated and are tabulated in Table III according to carbon type. It is apparent that the *ring carbons in the 2-position shift downfield upon complexation; those in the 5-position normally show even larger downfield shifts, while carbon 4 is variable with upfield or smaller downfield shifts.* The same trend is seen for the methyl carbons; methyl carbons on the nitrogen have relatively large downfield shifts. The nature of these $\Delta\delta$ shifts will be discussed below.

^1H NMR Spectra. The ^1H NMR resonances for these substituted imidazoles and their complexes in Me_2SO-d_6 are tabulated in Table IV. The assignments for the ring protons in the free ligands have been made by comparison with literature values and by assuming that the most downfield resonance is caused by the hydrogen on carbon 2, adjacent to two electronegative ring nitrogens. The assignments for 1-methylimidazole and 1,2-dimethylimidazole are made according to Takeuchi et al.,[5] and those of 1,4- and 1,5-dimethylimidazole are made according to Matthews and Rapoport.[7]

The assignments of the ligand protons in the complexes are made by paralleling the work of Storm et al.[8] based on the NOE enhancement of substituents at the C(4) position. The values in this report vary from those of Storm et al.[8] by small amounts; this may in fact be caused by differences in solvent (Me_2SO-d_6 vs. 1 M DCl), concentration, and instrumental variations. The differences are not severe enough to expect a change in proton assignments, and the trends in the $\Delta\delta_H$ values for the free ligands to those of the complexed ligands are consistent. The assignments for the complex with 2,4-dimethylimidazole have been made assuming the steric effect is such that the tautomer 2,5-dimethylimidazole is effectively bound to the cobalt center.

Table V contains the correlation of $\Delta\delta$ values of the proton resonances with the hydrogen type. It can be seen that the remote position (H(5)) and position H(2) have downfield shifts occurring upon complexation to the pentaamminecobalt(III) moiety. The H(4) proton undergoes a much smaller downfield shift. The hydrogen on the 2-position appears to be sensitive to the number of methyls substituted on the ring; two methyls cause a twofold

Table IV. ^1H NMR Shifts (δ) of Substituted Imidazoles and Their $(NH_3)_5Co^{3+}$ Complexes

	C(2)H	C(4)H	C(5)H	$CH_3(1)$	$CH_3(2)$	$CH_3(4)$	$CH_3(5)$
imidazole	7.68	7.04	7.04				
complex	8.12	7.15	7.57				
2-methylimidazole		6.84	6.84		2.25		
complex		6.94	7.41		2.34		
4-methylimidazole	7.48		6.69			2.12	
complex	7.93		7.21			2.10	
5-methylimidazole[a]	7.48	6.69					2.12
complex	7.96	6.85					2.26
1-methylimidazole	7.57	6.88	7.10	3.64			
complex	8.04	7.10	7.54	3.80			
1,2-dimethylimidazole		6.69	6.99	3.52	2.25		
complex		6.85	7.45	3.66	2.31		
1,4-dimethylimidazole	7.42		6.77	3.57		2.08	
complex	8.39		7.11	3.67		2.08	
1,5-dimethylimidazole	7.49	6.65		3.51			2.14
complex	8.51	7.19		3.66			2.23
2,5-dimethylimidazole[b]		6.51			2.19		2.05
complex		6.60			2.28		2.18

[a] Tautomer of 4-methylimidazole. [b] Tautomer of 2,4-dimethylimidazole.

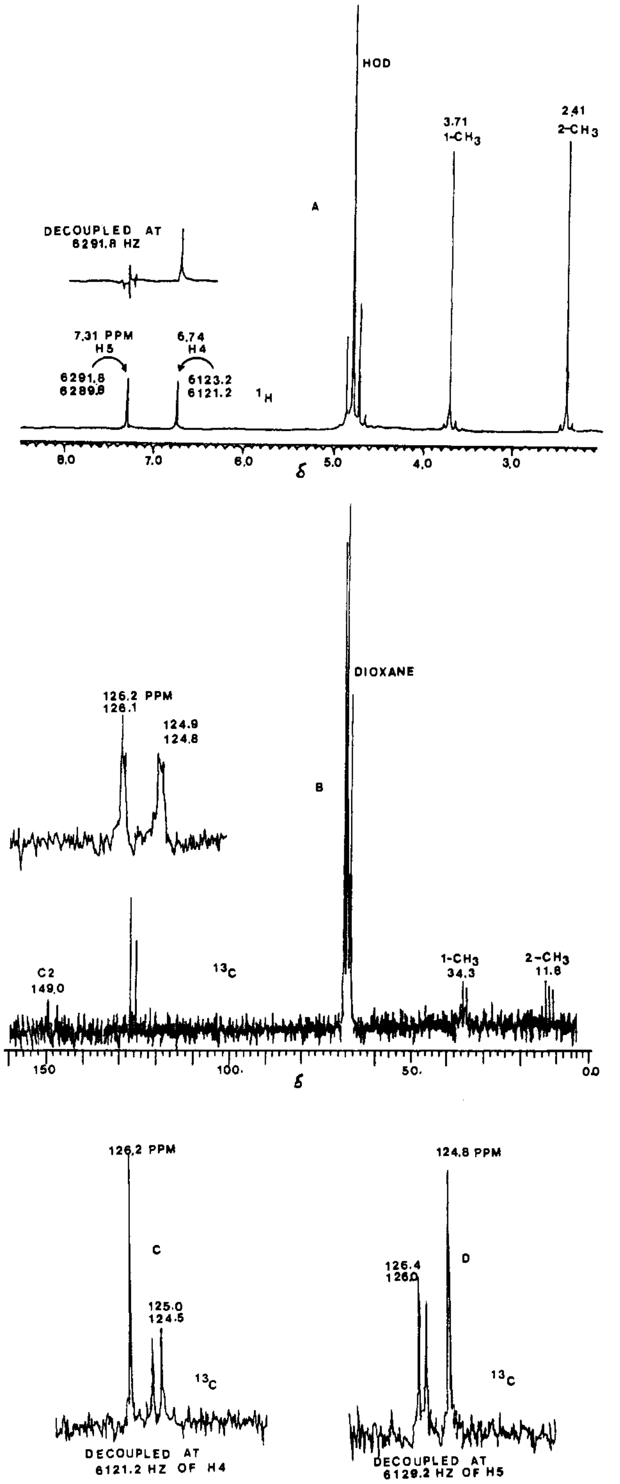


Figure 1. Proton saturation decoupling study of $Co(NH_3)_5(1,2\text{-}Me_2im)^{3+}$: (A) ^1H spectrum; (B) ^{13}C spectrum; (C) effect of saturation of the downfield ^1H resonance (H(4)) in the ^{13}C spectrum; (D) effect of saturation of the upfield ^1H resonance (H(5)) in the ^{13}C spectrum.

increase in the downfield shift compared to the monomethyl cases. The methyl hydrogens follow the same trends; $CH_3(2)$ and $CH_3(5)$ have small downfield shifts, and $CH_3(4)$ have very small downfield (and even upfield) shifts. Methyl hydrogens on nitrogen N(1) also show downfield shifts.

Table V. Correlation of ^1H $\Delta\delta$ Values by Hydrogen Type[a]

C(4)H	-0.11, -0.10, -0.16, -0.22, -0.16, -0.54, -0.09
$C(4)CH_3$	+0.02, +0.00
C(5)H	-0.53, -0.57, -0.52, -0.44, -0.46, -0.34
$C(5)CH_3$	-0.14, -0.09, -0.13
C(2)H	-0.44, -0.45, -0.48, -0.47, -0.97, -1.02
$C(2)CH_3$	-0.09, -0.06, -0.09
$N(1)CH_3$	-0.16, -0.14, -0.10, -0.15

[a] Negative value denotes a downfield shift. Positive value denotes an upfield shift (relative to free-ligand value of δ upon coordination).

Table VI. ^1H NMR Chemical Shifts (δ) for 1-Methylimidazole Complexes

	H(2)	H(5)	H(4)
LD^+	8.65	7.43	7.41^a
$Co(NH_3)_5L^{3+}$	8.02	7.38	7.08^b
$HgCH_3L^+$	7.84	7.24	7.08^a
$Co(CN)_5L^{2-}$	7.76	7.02	7.02^a
$Ru(NH_3)_5L^{2+}$	7.59	7.16	6.96^a
$Fe(CN)_5L^{3-}$	7.63	7.07	6.86^a
L = 1-MeIm	7.57	7.07	6.99^c

[a] Reference 3. [b] Reference 8. [c] Reference 5.

Table VII. $\Delta\delta$ Values for 1-Methylimidazole Complexes[a]

	H(2)	H(5)	H(4)
LD^+	-1.08	-0.36	-0.42
$Co(NH_3)_5L^{3+}$	-0.45	-0.31	-0.09
$HgCH_3L^+$	-0.27	-0.17	-0.09
$Co(CN)_5L^{2-}$	-0.19	+0.05	-0.03
$Ru(NH_3)_5L^{2+}$	-0.02	-0.09	+0.03
$Fe(CN)_5L^{3-}$	-0.06	0	+0.13

[a] Negative value denotes a downfield shift; positive value denotes an upfield shift (relative to the free-ligand δ upon coordination).

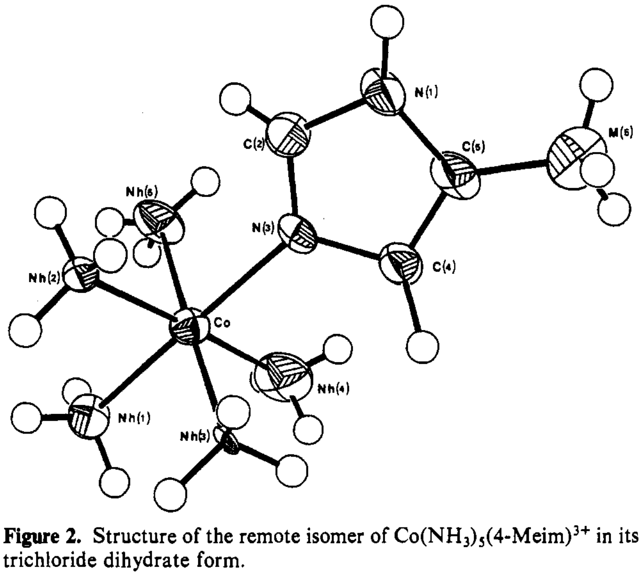


Figure 2. Structure of the remote isomer of $Co(NH_3)_5(4\text{-}Meim)^{3+}$ in its trichloride dihydrate form.

^1H NMR Spectra of 1-Methylimidazole Complexes. In an earlier report[3] the ^1H chemical shift changes upon complexation of 1-methylimidazole to various metal centers were given, along with a discussion of the factors influencing those changes. The assignments of the protons in the complexes were made assuming that the most upfield chemical shift was caused by the remote proton, H(5); this assignment was made based on several literature protocols. However, this assignment has been shown to be incorrect by the NOE experiments of Storm et al.[8] for at least the pentaamminecobalt(III) complex. Takeuchi et al. also have the H(4) proton upfield of the H(5) proton in the free ligand.[5] Assuming that the other complexes of ref 3 behave similarly, the chemical shifts have been retabulated in Table VI and the chemical shift changes are shown in Table VII.

The general trend for 1-methylimidazole complexes is for the adjacent H(4) proton to have a smaller shift downfield than the remote H(5) proton upon complexation. This is the same trend observed in the ^1H NMR spectra of the cobalt substituted-imidazole complexes reported here. A further observation is noted; the shift changes of the ring protons become less in the downfield direction as the σ-withdrawal to the metal decreases, and the H(4)

Table VIII. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$)

	x	y	z	U
Co	1556 (1)	844 (1)	0	26 (1)[a]
Nh(1)	2237 (2)	–416 (4)	64 (26)	35 (2)[a]
Hn(1a)	2631	10	181	161 (43)
Hn(1b)	2230	–893	–1101	110 (52)
Hn(1c)	2181	–977	1126	222 (84)
Nh(2)	1145 (3)	–129 (5)	1994 (9)	26 (2)[a]
Hn(2a)	853	–704	1426	0 (13)
Hn(2b)	928	433	2839	109 (40)
Hn(2c)	1452	–598	2699	436 (98)
Nh(3)	1995 (4)	1807 (10)	2040 (14)	20 (3)[a]
Hn(3a)	1701	2052	3004	41 (22)
Hn(3b)	2184	2548	1500	307 (85)
Hn(3c)	2313	1284	2599	160 (65)
Nh(4)	1998 (7)	1773 (19)	–1945 (20)	59 (6)[a]
Hn(4a)	1810 (41)	2390 (97)	–2491 (140)	47 (28)
Hn(4b)	2261 (33)	2256 (67)	–1385 (100)	19 (18)
Hn(4c)	2113 (39)	1385 (71)	–2661 (92)	1 (20)
Nh(5)	1104 (3)	–97 (7)	–2029 (10)	44 (2)[a]
Hn(5a)	1131 (28)	–737 (50)	–1815 (87)	2 (16)
Hn(5b)	850 (22)	362 (44)	–2723 (72)	0 (12)
Hn(5c)	1386 (31)	–406 (63)	–2760 (99)	21 (19)
N(3)	898 (2)	2107 (4)	–169 (18)	24 (2)[a]
C(4)	985 (3)	3426 (5)	–62 (34)	37 (2)[a]
Hc(4)	1400 (22)	3862 (44)	571 (73)	8 (14)
C(5)	415 (3)	3988 (5)	–2 (27)	41 (2)[a]
M(5)[b]	231 (4)	5373 (6)	–53 (29)	65 (3)[a]
Hm(5a)[c]	540	5842	–749	37 (21)
Hm(5b)	202	5696	1223	1094 (116)
Hm(5c)	–167	5458	–673	136 (49)
N(1)	–16 (2)	3030 (5)	32 (23)	41 (2)[a]
Hn(1)	–434 (27)	3058 (48)	423 (100)	24 (17)
C(2)	298	1930 (5)	79 (31)	34 (2)[a]
Cl(1)	7626 (1)	533 (1)	–6 (9)	42 (1)[a]
Cl(2)	172 (1)	1381 (1)	4993 (10)	42 (1)[a]
Cl(3)	6454 (1)	–1290 (2)	4974 (26)	144 (2)[a]
W(1)	6315 (2)	1758 (4)	5029 (27)	54 (2)[a]
Hw(1a)	968 (29)	2933 (62)	4964 (300)	72 (22)
Hw(1b)	6300 (34)	998 (64)	4752 (217)	80 (29)
W(2)	1626 (6)	–2854 (12)	–195 (74)	253 (15)[a]
Hw(2a)	6727 (21)	–2105 (43)	11147 (72)	0 (12)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] M = methyl carbon. [c] Hm = methyl hydrogen.

Table IX. Bond Lengths[a] (Å)

Co–Nh(1)	1.976 (5)	Co–Nh(2)	1.947 (6)
Co–Nh(3)	1.992 (10)	Co–Nh(4)	1.930 (16)
Co–Nh(5)	1.989 (7)	Co–N(3)	1.945 (5)
Nh(4)–Hn(4a)	0.856 (102)	Nh(4)–Hn(4b)	0.856 (69)
Nh(4)–Hn(4c)	0.694 (74)	Nh(5)–Hn(5a)	0.695 (54)
Nh(5)–Hn(5b)	0.876 (49)	Nh(5)–Hn(5c)	0.857 (69)
Hn(5a)–Hn(5c)	0.927 (90)	N(3)–C(4)	1.410 (7)
N(3)–C(2)	1.311 (8)	C(4)–Hc(4)	1.095 (48)
C(4)–C(5)	1.360 (9)	C(5)–M(5)[a]	1.518 (9)
C(5)–N(1)	1.371 (8)	N(1)–Hn(1)	0.937 (58)
N(1)–C(2)	1.344 (7)	C(2)–H(2)	0.874 (59)
W(1)–Hw(16)	0.828 (82)	Hw(1a)–W(1a)	0.814 (75)
Hw(2a)–W(2a)	0.967 (71)		

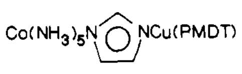
[a] M = methyl carbon.

Table X. Bond Angles (deg)

Nh(1)–Co–Nh(2)	87.8 (4)	Nh(1)–Co–Nh(3)	88.8 (5)
Nh(2)–Co–Nh(3)	88.2 (3)	Nh(1)–Co–Nh(4)	89.8 (7)
Nh(2)–Co–Nh(4)	177.4 (5)	Nh(3)–Co–Nh(4)	90.9 (6)
Nh(1)–Co–Nh(5)	92.2 (4)	Nh(2)–Co–Nh(5)	91.7 (3)
Nh(3)–Co–Nh(5)	179.0 (3)	Nh(4)–Co–Nh(5)	89.3 (5)
Nh(3)–Co–N(3)	92.0 (4)	Nh(4)–Co–N(3)	87.9 (6)
Nh(1)–Co–N(3)	177.6 (6)	Nh(2)–Co–N(3)	94.5 (3)
Nh(5)–Co–N(3)	87.0 (3)	Co–Nh(4)–Hn(4a)	118.2 (60)
Co–Nh(4)–Hn(4b)	107.6 (51)	Hn(4a)–Nh(4)–Hn(4b)	93.4 (85)
Co–Nh(4)–Hn(4c)	112.6 (62)	Hn(4a)–Nh(4)–Hn(4c)	107.1 (88)
Hn(4b)–Nh(4)–Hn(4c)	116.9 (88)	Co–Nh(5)–Hn(5a)	106.9 (51)
Co–Nh(5)–Hn(5b)	114.9 (32)	Hn(5a)–Nh(5)–Hn(5b)	135.4 (61)
Co–Nh(5)–Hn(5c)	106.0 (46)	Hn(5a)–Nh(5)–Hn(5c)	72.5 (67)
Hn(5b)–Nh(5)–Hn(5c)	108.4 (55)	Nh(5)–Hn(5a)–Hn(5c)	61.9 (62)
Nh(5)–Hn(5c)–Hn(5a)	45.7 (47)	Co–N(3)–C(4)	125.4 (4)
Co–N(3)–C(2)	127.2 (5)	C(4)–N(3)–C(2)	105.3 (5)
N(3)–C(4)–Hc(4)	123.1 (27)	N(3)–C(4)–C(5)	108.3 (5)
Hc(4)–C(4)–C(5)	122.2 (27)	C(4)–C(5)–M(5)	130.9 (6)
C(4)–C(5)–N(1)	106.4 (5)	M(5)–C(5)–N(1)	122.6 (6)
C(5)–N(1)–Hn(1)	128.7 (32)	C(5)–N(1)–C(2)	107.6 (4)
Hn(1)–N(1)–C(2)	119.9 (32)	N(3)–C(2)–N(1)	111.3 (5)
N(3)–C(2)–H(2)	118.4 (37)	N(1)–C(2)–H(2)	125.5 (35)

and H(5) protons can shift upfield in the cases where the metal is considered to be a good π-donor.

Structure of [Co(NH$_3$)$_5$(4-MeIm)]Cl$_3$·2H$_2$O. The ORTEP drawing of the complex ion is shown in Figure 2. Positional parameters are listed in Table VIII. It is clear that the point of attachment of the methyl group to the imidazole ring is the remote carbon, C(5). The imidazole ring is twisted with respect to the two planes created by the near-octahedral geometry of the complex. The angle that the plane of the imidazole ring makes with the Nh(1)–Nh(2)–Nh(4)–Co–N(3) plane is 43.6° while the angle with the Nh(1)–Nh(3)–Nh(5)–Co–N(3) plane is 41.9° (Nh = ammonia nitrogen). These angles are close to those expected (45°) solely upon the basis of steric interactions with the cis ammonia ligands. Storm et al. report twist angles of 44.2 and 47.9° in the 4-nitroimidazolato complex of Co(NH$_3$)$_5$$^{3+}$,[14] and Davis et al. reported that the Co dihedral angles are approximately 45° in the complex[15]



The close agreement of these twist angles to 45° give evidence that π-back-bonding interactions between the Co and the imidazole rings in these complexes are not important.

The bond lengths for the title complex are listed in Table IX, and the bond angles are listed in Table X. The cobalt–cis-nitrogen bond lengths range from 1.930 (16) to 1.992 (10) Å with an average length of 1.96 Å; the cobalt–trans-nitrogen bond length, Co–Nh(1), is 1.976 (5) Å. There is no apparent trans effect in the complex. Storm et al. report a "small but significant" shortening of the trans-NH$_3$–Co bond in the 4-nitroimidazolato complex evidenced by the trans-N–Co bond distance of 1.966 (2) Å compared to the average cis-N–Co distance of 1.972 (2) Å.[14] There is no trans influence in the imidazolato-bridged Co–Cu binuclear ion of Davis et al., as indicated by the Co–N bond lengths.[15] The lack of significant trans effects in complexes of this type supports the conclusion that π-interactions between the cobalt center and the imidazole ligand are not important.

The rest of the bond distances and bond angles in the complex are not at significant variance with those expected based upon similar complexes. The temperature factors for one of the ammonia nitrogen atoms (Nh(3)) are very different from those of the other ammonia nitrogens. The possibility of an incorrect atom assignment is eliminated by the details of the synthetic method and by the appearance of the proper Co–N bond distance.

Discussion

The many factors influencing the NMR chemical shifts of protons and carbon-13 atoms in nitrogen heterocycles coordinated to metal centers have been discussed by several research groups,[1–4,9–13] yet no consensus has been reached pertaining to the dominant mechanism. The most commonly invoked reasoning deals with bond polarization caused by σ-withdrawal of electron density via the nitrogen lone pair and π-back-bonding from the

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metal d orbitals to the ligand π^* orbitals. The σ-effect yields downfield shifts at all positions as a result of inductive decrease in e^- density; however, the downfield shift should attenuate with distance. Where π-back-bonding is possible, an upfield contribution should be present. This shift will be manifested about the heterocyclic ring in a manner determined by the atomic orbital character of the π^* orbital into which the back-bonding occurs. The π-effect does not attenuate with distance and is expected to predominate at moderate distances from the metal center. These two effects rarely suffice to explain all the NMR data.

Malin et al. have postulated that magnetic anisotropy of the cyanide spectator ligands leads to downfield shifts in the α-carbon and hydrogen NMR spectra in $Fe(CN)_5^{3-}$ complexes with 6-membered azines.[10] This effect is caused by the electrons circulating in the C≡N triple bonds and depends upon the distance and orientation of the magnetic nuclei from the cyanides. The use of ammonia ligands as the spectator set in this study precludes this mechanism from consideration.

Another possible effect of the metal center is related to residual paramagnetism. This results from excited-state mixing of paramagnetic ^1E and $^1A_2$ states into the diamagnetic $^1A_1$ ground state of complexes with reduced C_{4v} symmetry.[2] The magnitude and direction of the shift depends upon the identity of the ML_5^{n+} fragment and the distance and angle of the magnetic nucleus from the metal. The effect usually gives shielding contributions to nuclei in coordinated heterocycles, but the effect is smaller for ammonia vs. cyanide spectator ligands. This results because the position of most heterocycles within the spectrochemical series is closer to ammonia than cyanide.[2] Hence, the distortion in the cyano complexes allows for a greater increase in excited-state mixing.

Another possible shift mechanism is related to the σ and π bond orders between the atoms in the heterocyclic ring. Pugmire and Grant[12,13] explain the ^{13}C $\Delta\delta$ values for the α-carbons in pyridine and imidazole upon protonation by showing that extended Hückel and SCF calculations predict a decrease in the π-electron overlaps between the N and C_α atoms. This gives rise to an upfield shift; there is a similar effect with σ-overlap populations, but it appears to be of a smaller magnitude. These effects do not influence the NMR shifts of protons on the ring; α-protons shift downfield upon coordination to H^+.

Three other effects are worth noting: solvent effects, quadrupolar broadening caused by the metal, and magnetic anisotropy of the metal–ligand bond. Solvents can cause substantial shifts resulting from their interaction with the nitrogen lone pair of the heterocycles. These shifts should parallel those resulting from protonation of the ligand and are of more importance in rationalizing ^1H shifts than ^{13}C shifts.[1] The use of Me_2SO-d_6, a less polar solvent than D_2O, in the ^1H NMR samples helps reduce the magnitude of the solvent effects.

Lavallee and Fleischer report a lessening in the intensity of the α-proton resonances in $Ru(NH_3)_5py^{2+}$ as a result of the quadrupolar interaction with the Ru metal center.[11] The α-resonances are integrated to only 70% of the β-resonances, a result explained by assuming that the H_α–Ru spin–spin interaction with the 29.8% of Ru which has a $^5/_2$ nuclear spin broadens that portion of the proton resonance. The effect at the β-positions is negligible because of the r^{-3} dependence of the interaction. Quadrupole broadening, while possible for cobalt complexes, appears to be less of a problem. No lessening of the adjacent nuclear resonances was seen in any of the complexes.

The possibility of magnetic anisotropy in the metal–ligand bond was discussed in Foust and Ford's paper on the shifts in organonitrile complexes.[9] They concluded that these effects were of minimal importance; the effects seen for imidazole type ligands, which are less likely to have resonance structures with multiple-bond character in the metal–ligand bonds, will be of even less importance.

The trend in the $\Delta\delta$ values for the ^{13}C NMR resonances in pentaamminecobalt(III) imidazoles occurs so that the carbons in positions 2 and 5 are shifted downfield upon coordination and carbon 4 is either shifted upfield or displays a much smaller downfield shift. Rings with C(2)-methylation show large downfield shifts of carbon 4. The shifts for the 2- and 5-positions are explainable as a superposition of σ-donation and π-back-bonding effects upon those carbons, keeping in mind the relatively poor π-back-bonding ability of the Co(III) center. These arguments have been presented before by several authors in describing the effects upon the β- and γ-carbons of pyridines[1,2,10] coordinated to a variety of metal centers and in substituted imidazole and pyrazole complexes.[3]

The carbon at position 4, the adjacent carbon, is more difficult to understand. The effects of σ-donation and π-back-bonding are still present and lead to a downfield contribution to the $\Delta\delta$ values. The trend is toward upfield for C(4) in these cobalt complexes; hence, there is at least one major upfield contribution to be considered. Lavallee et al. find upfield shifts at the adjacent positions in pyridine complexes where the coordinating moiety is H^+ and increasingly downfield shifts for CoA_5^{3+}, RuA_5^{2+}, and $Fe(CN)_5^{3-}$.[1] They suggest that the σ-donation effect at the α-carbon is compensated by a shift in electron density from the β-carbon. The net electron density at the α-carbon remains the same, yet the anisotropy of the density is different. Their proton data have the opposite trend and is explained by assuming that the electron density in the carbon–hydrogen bonds is insulated from these compensating polarization effects between α- and β-carbons. The data for the cobalt imidazole compounds presented in this paper indicate that the trend in shifts for the proton resonances is nearly the same as those for the ^{13}C NMR. Thus, this polarization/compensation argument appears to be at most a minor effect.

The effect of temperature-induced paramagnetism has been discussed in regard to both ^1H and ^{13}C NMR data in a number of similar cases.[1,2,10,11] These studies included Ru, Rh, Fe and Co as metal centers and indicate upfield shifts at all adjacent positions. Ford and Foust discount the importance of TIP of Ru and Rh on organonitrile ^1H resonances because the ortho positions are all shifted downfield.[9] The TIP effect is distance-sensitive, and the proton positions in these compounds may have been out of range; however, the adjacent 2-position in the imidazoles of the present study are also shifted downfield. (Slightly less on average than C(5): −3.38 for C(2); −4.83 for C(5), excluding $2\text{-}CH_3$ substitution cases.) The conclusion must be that the residual paramagnetism of the cobalt center is not dominant. Rings with C(2)-methylation show small upfield shifts for C(5). Thus C(2) methylation reverses the dominant downfield trend at C(5) and the upfield trend at C(4).

When pyridines and imidazoles are protonated, the ^{13}C chemical shifts of the α-carbons move upfield and the β- (and γ-) carbons move downfield. Pugmire and Grant[12,13] explain this by using theoretical calculations and σ- and π-electron densities and bond orders. They note a decrease in π bond order in the N–C_α bond whenever the α-carbon chemical shift is shielded upon protonation. Apparently, coordination to Co(III) causes the same effect upon imidazole type ligands. This effect at the adjacent carbon 4 positions is upfield and is of larger magnitude than the downfield shift expected from σ-electron induction. Pugmire and Grant's effect causes a small upfield shift at carbon 2 and a downfield shift at carbon 5; neither expectation conflicts with the observed trend for cobalt imidazole complexes.

The chemical shift changes of methyl carbons behave in the same manner as the carbon to which they are attached but with a smaller magnitude. (The 1,5-dimethylimidazole case is an exception for C(5).) Factors that influence the electron density at the carbons might be expected to affect the substitutent nuclei as a result of induction. Changes in the π bond order at the α-carbon would not necessarily affect the methyl groups substituted at the adjacent position. The trends indicate that the methyl carbons are sensitive to the π bond order; a rehybridization of the α-carbon atomic orbitals may account for this. The extent of hyperconjugation of the methyl substitutent could be coupled to the degree of altered hybridization of the ring carbon and thus parallel the shift of its ring carbon.

It should be also noted that substitution of C(5) causes more sensitivity in the final ^{13}C shifts than substitution at C(4), where multiple influences of the metal center, altered hybridization upon coordination, and any TIP influence moderates the substituent influence relative to an H substituent on C(4).

The trends for the ^{1}H NMR chemical shift differences are similar to those of the ^{13}C NMR experiments. The hydrogens at the remote 5-position and the 2-position are shifted downfield as a result of σ-electron polarization without effective π-backbonding. The protons at the adjacent position are subject to the same considerations as a methyl group substituted at C(4). Lavallee et al.[1] attribute the upfield shifts of α-protons in substituted pyridines complexed to CoA_5^{3+}, RhA_5^{3+}, and RuA_5^{2+} to a TIP effect (A = NH_3). Work with other 6-membered azines with RuA_5^{2+} and RhA_5^{3+} has been likewise interpreted.[11] These effects apparently are not applicable here since hydrogens at the 2-position, also adjacent to the cobalt center, are shifted downfield.

The trend at H(4) upon coordination of an imidazole can be rationalized by assuming that there are π bond order changes within the heterocycle and that these changes occur with rehybridization of the ring carbons. The substituents on the ring will then exhibit subsequent changes in electron density, leading to small upfield shifts at the 4-position and downfield shifts at the 5-position. The upfield shift in the adjacent position is apparently of small magnitude and does not cancel the downfield effect of σ-polarization.

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Registry No. $[Co(NH_3)_5(4\text{-Meim})]Cl_3{\cdot}2H_2O$, 103203-21-0; $[Co(NH_3)_5(2\text{-Meim})]^{3+}$, 89955-97-5; $[Co(NH_3)_5(4\text{-meim})]^{3+}$, 89955-98-6; $[Co(NH_3)_5(5\text{-Meim})]^{3+}$, 103302-00-7; $[Co(NH_3)_5(1\text{-Meim})]^{3+}$, 91209-43-7; $[Co(NH_3)_5(1,2\text{-Me}_2\text{im})]^{3+}$, 91209-45-9; $[Co(NH_3)_5(1,4\text{-Me}_2\text{im})]^{3+}$, 103203-22-1; $[Co(NH_3)_5(1,5\text{-Me}_2\text{im})]^{3+}$, 103203-23-2; $[Co(NH_3)_5(2,5\text{-Me}_2\text{im})]^{3+}$, 103203-24-3; imidazole, 288-32-4; 2-methylimidazole, 693-98-1; 4-methylimidazole, 822-36-6; 1-methylimidazole, 616-47-7; 1,2-dimethylimidazole, 1739-84-0; 1,4-dimethylimidazole, 6338-45-0; 1,5-dimethylimidazole, 10447-93-5; 2,4-dimethylimidazole, 930-62-1.

Supplementary Material Available: Table of anisotropic temperature factors (1 page). Ordering information is given on any current masthead page.

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Molecular Structures of Zinc Dichloride, Zinc Dibromide, and Zinc Diiodide from Electron Diffraction Reinvestigation

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The molecular structures of zinc dichloride, zinc dibromide, and zinc diiodide have been determined at approximately 656, 614, and 580 K, respectively, by gas-phase electron diffraction. The analysis was paralleled by spectroscopic calculations. When the consequences of perpendicular vibrations are accounted for, all molecules display linear configurations with the following bond lengths (r_g): Zn–Cl = 2.072 ± 0.004 Å, Zn–Br = 2.204 ± 0.005 Å, and Zn–I = 2.401 ± 0.005 Å.

Introduction

The present investigation of the molecular structure of zinc dihalides was initiated in order to augment our electron diffraction studies of first-row transition-metal dihalides, viz. VCl_2,[1] $CrCl_2$,[1] $MnCl_2$,[2] $MnBr_2$,[3] $FeCl_2$,[4,5] $FeBr_2$,[4] $CoCl_2$,[6] $CoBr_2$,[7] and $NiBr_2$.[8] The structure of $NiCl_2$ was determined in Professor Hedberg's laboratory.[9] Another investigation[10] is under way concerning the molecular structure of $CaCl_2$, $CaBr_2$, and CaI_2. While calcium is not a transition metal, this work is an extension of the above studies.

Determination of the structures of these apparently simple symmetric molecules is not always easy. The temperatures required for their volatilization (800–1300 K)[1-8] may lead to reaction with nozzle material or to the formation of dimers.[1,3,4,7] Also, these high temperatures excite large-amplitude bending vibrations that make determination of the equilibrium symmetries difficult. Mass spectrometric control and optimization of the electron diffraction experimental conditions have considerably facilitated these studies.[11]

The structures of $ZnCl_2$, $ZnBr_2$, and ZnI_2 were studied[12] by electron diffraction nearly 30 years ago, but the authors were not able to determine with certainty whether or not the equilibrium configuration of the molecules was linear. Improvements in the method, which include use of spectroscopic data, now permit more accurate analyses of such structures. Since the equilibrium configuration of the molecules is an important question, the structures have been reinvestigated by making use of spectroscopic data that have become available in the meantime.[13,14]

Experimental Section

For all three compounds commercial samples were used. The electron diffraction patterns were recorded in our modified EG-100A apparatus[15] with a nozzle[16] of stainless steel. Quadrupole mass spectrometric measurements under the conditions of the electron diffraction experiments revealed no detectable amounts of dimeric species. Some of the electron diffraction experimental conditions are summarized in Table I. Other experimental conditions and data processing were the same as in the other studies of the series. Listings of total electron diffraction intensities are available as supplementary material. The electron scattering factors for

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