all of the above mentioned pathways. The complexity of the $Ni(H_{-2}GGHis)^-$ reactions arises because several of the pathways can simultaneously contribute to the rate of the observed dissociation reaction. Also, within each pathway, the location of the rate-determining step is very dependent on the reaction conditions.

At pH 5–7 the $Ni(H_{-2}GGHis)^-$ complex reacts with acid and the rate expression contains both $[H^+]^2$ and $[H^+][HB]$ terms. This is illustrated by the slope of −2 in Figure 1 and the complex acetic acid dependence in Figure 5. This kinetic behavior is accounted for by the proton-assisted general-acid reaction pathway in which the protonation of the $Ni(H_{-1}GGHis)$ is rate limiting (D → E in Figure 2). When either or both of the general-acid and H^+ concentrations is increased, the rate-limiting step is shifted to an earlier point in the reaction sequence. Under such circumstances the dissociation rate is carried by a combination of the inside-protonation and outside-protonation pathways. At higher $[H^+]$ there is kinetic evidence for the formation of two outside-protonated species (D and C in Figure 2) with protonation constants of $10^{4.3}$ and $10^{1.3}$ M^{-1}. Below pH 5 the dissociation reaction proceeds exclusively by the specific-acid catalyzed outside-protonation pathway (Figure 2). Even in the pH 5–7 region, H_3O^+ preferentially reacts via the outside-protonation pathway, although general acids, HB, such as acetic acid react via the inside-protonation pathway (A → D in Figure 2). This conclusion is based on the observation that the ratio of the H_3O^+ rate constant ($K_{1H}k_{1d}$) to the general-acid rate constants (k_{1HB}) for the $Ni(H_{-2}GGHis)^-$ reactions are more than 1 order of magnitude greater than has been observed for the reactions of $Ni(H_{-2}G_3)^-$ [1,4] and other metal–peptide complexes.[16,17]

The nucleophilic reaction of trien with $Ni(H_{-2}GGHis)^-$ is more than 5 orders of magnitude slower than the analogous reaction with $Ni(H_{-2}G_3)^-$. Furthermore, between pH 6 and pH 8 a proton-assisted nucleophilic pathway with $H_2(trien)^{2+}$ is evident (Figure 2). In both of these respects the trien reactions with $Ni(H_{-2}GGHis)^-$ are very similar to the analogous $Cu(H_{-2}GGHis)^-$ reactions.[8,9]

Acknowledgment. This investigation was supported by National Science Foundation Grant CHE74-00043 and National Institutes of Health Grant GM19775.

Registry No. $Ni(H_{-2}GGHis)^-$, 62006-82-0; trien, 112-24-3; glycine, 56-40-6; HCOOH, 64-18-6; HOAc, 64-19-7; NH_2OH, 7803-49-8.

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Investigation of the Axial Ligand Binding Reactions of (*meso*-Tetraphenylporphinato)magnesium(II) with Nitrogenous Bases

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Received June 15, 1981

The stability constants of the complexation reactions of (*meso*-tetraphenylporphinato)magnesium(II) ((TPP)Mg) with nitrogenous bases were calculated by the computer program SQUAD. This program processed the spectral data without any assumption; it provided more accurate results than those obtained from a Benesi–Hildebrand plot. The calculations yielded values for the stepwise stability constants of ML and ML_2. The stability constants are linear functions of the ligand pK_a, which were similar to (TPP)Zn results. The different trends of log K_1 and log K_2 with the ligand pK_a were explained.

Almost 30 years ago Miller and Dorough[1] measured the stability constants for addition of pyridine to (*meso*-tetraphenylporphinato)magnesium(II) ((TPP)Mg) in benzene. Fourteen years later a similar study was performed by Storm et. al.[2] using 2,6-lutidine as solvent. Two steps of axial ligand (L) addition to (TPP)Mg(M) are possible. The first step is the formation of the 1:1 complex (eq 1) and the second is the 1:2 complex (eq 2). Both studies found a close resemblance of the optical absorption spectra between uncomplexed (TPP)Mg and the monopyridinate complex and observed that (TPP)Mg(py) was never completely converted to the dipyridinated complex $(TPP)Mg(py)_2$. The facts that both the uncomplexed species and the monoadduct have almost identical spectra and that a very stable monopyridinate complex is followed by a very weak dipyridinate complex make calculations of stability constants from spectral curves difficult. Because of this difficulty, only a single value of ligand addition has ever been published for reaction 1 and reaction 2.

$$M + L \overset{K_1}{\rightleftharpoons} ML \qquad \beta_1 = K_1 \tag{1}$$

$$ML + L \overset{K_2}{\rightleftharpoons} ML_2 \qquad \beta_2 = K_1K_2 \tag{2}$$

In our laboratory we have found a way to determine these stability constants by using a computer program, SQUAD (stability quotients from absorbance data).[3] This program has been set up to search for the best combination of stability constants that will describe the supplied data. A maximum of two metals, of two ligands, and of six unknown stability constants can be handled simultaneously by SQUAD and stability constants determined from small spectral differences between the complexed and uncomplexed species.

In this paper, we wish to present measured stability constants of (TPP)Mg complexed with 18 different nitrogenous bases under 0.1 M tetrabutylammonium perchlorate (TBAP) in methylene chloride (CH_2Cl_2).

Experimental Section

Materials. Free base 5,10,15,20-tetraphenylporphyrin ($(TPP)H_2$) was prepared by the method of Adler[4] and purified by the method of Barnett et al.[5] Mg(II) was inserted into $(TPP)H_2$ by essentially the method of Adler et al.,[6] with $Mg(C_2H_3O_2)_2$ in place of $MgCl_2$

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(1) Miller, J. R.; Dorough, G. D. *J. Am. Chem. Soc.* **1952**, *74*, 3977.

(2) Storm, C. B.; Corwin, A. H.; Arellano, R. R.; Martz, M.; Weintraub, R. *J. Am. Chem. Soc.* **1966**, *88*, 2525.

(3) Leggett, D. J.; McBryde, W. A. E. *Anal. Chem.* **1975**, *47*, 1065.

(4) Adler, A. D. *J. Org. Chem.* **1967**, *32*, 476.

(5) Barnett, G. H.; Hudson, M. F.; Smith, K. M. *J. Chem. Soc., Perkin Trans, 1* **1975**, *9*, 1401.

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Table I. Stability Constants for Addition of Ligands to (TPP)Mg To Form (TPP)Mg(L) and $(TPP)Mg(L)_2$ in 0.1 M $TBAP/CH_2Cl_2$

no.	ligand	pK_a[a]	$\log \beta_1$	$\log \beta_2$	$\log K_2$[b]
1	3,5-dichloropyridine	0.67	1.88 ± 0.04[c]	1.74 ± 0.06[c]	−0.14
2	3-cyanopyridine	1.45	2.20 ± 0.03	2.26 ± 0.03	0.16
3	4-cyanopyridine	1.86	2.33 ± 0.06	2.31 ± 0.06	−0.02
4	3-chloropyridine	2.81	2.49 ± 0.05	2.39 ± 0.05	−0.10
5	3-bromopyridine	2.84	2.63 ± 0.04	2.27 ± 0.05	−0.36
6	3-acetylpyridine	3.18	3.26 ± 0.04	3.04 ± 0.04	−0.22
7	4-acetylpyridine	3.51	3.38 ± 0.04	3.16 ± 0.05	−0.22
8	pyridine (4-H)	5.29	3.63 ± 0.04	2.90 ± 0.04	−0.73
9	3-picoline	5.79	4.19 ± 0.05	3.34 ± 0.07	−0.85
10	4-picoline	5.98	4.21 ± 0.06	3.41 ± 0.06	−0.80
11	3,4-lutidine	6.46	4.23 ± 0.06	3.34 ± 0.07	−0.89
12	1-methylimidazole	7.33	5.40 ± 0.07	4.44 ± 0.07	−0.96
13	piperidine	11.1	4.33 ± 0.04	3.81 ± 0.05	−0.52
14	2-picoline	5.96	2.47 ± 0.05	2.27 ± 0.09	−0.20
15	2-aminopyridine	6.82	3.05 ± 0.08	2.89 ± 0.13	−0.16
16	2-methylimidazole	7.56	5.76 ± 0.42	9.91 ± 0.46	4.15
17	imidazole	6.65	4.98 ± 0.03	5.19 ± 0.10	0.21
18	4-(*N*,*N*-dimethylamino)pyridine	9.71	4.49 ± 0.04	4.78 ± 0.29	0.29

[a] From: Schoefield, K. S. "Hetero-Aromatic Nitrogen Compounds"; Plenum Press: New York, 1967; p 146. [b] $\log K_2 = \log \beta_2 - \log \beta_1$. [c] Values presented are standard deviations of the constants as calculated by the program. See: Tobias, R. S.; Hugus, Z. Z., Jr. *J. Phys. Chem.* 1961, *65*, 2165.

as salt and 3% methanolic KOH as catalyst.[7,8] The progress of the reaction was monitored spectrally. Eight hours were required for complete incorporation of Mg^{2+} into the hole of the porphyrin. The crude product was purified by chromatography on basic alumina (Brockman activity 1, 80–200 mesh) with acetone. The eluate of the purple band was collected as pure (TPP)Mg. Purified (TPP)Mg had the same optical absorption spectrum as that reported by Miller and Dorough.[1] During the preparation of (TPP)Mg, it is possible that a water molecule could be introduced into the porphyrin forming aquomagnesium tetraphenylporphyrin.[9] So that this possibility could be eliminated, purified (TPP)Mg was measured thermogravimetrically with a Perkin-Elmer TGS-2, in conjunction with a model AR-2 autobalance, model UU-1 temperature programmer, and Linear Instrument Co. strip chart recorder. About 3% mass loss at 200 °C was detected, which is equivalent to 1 mol of water/porphyrin molecule. Because of this, each porphyrin was placed in the oven at 200 °C 1 h before each spectrophotometric measurement.

The supporting electrolyte, TBAP, was obtained from Eastman Chemical, recrystallized once from either ethyl acetate/pentane or CH_2Cl_2/ether, and put in the vacuum oven at 40 °C prior to use. The 18 different nitrogenous bases used as ligands were obtained from Fisher Scientific or Aldrich Chemical and were purified by standard literature methods.[10] The solvent, CH_2Cl_2, was reagent grade, double distilled from P_2O_5, and stored over 4-Å Linde molecular sieves prior to use.

Methods of Calculation. Stability constants, $\log \beta_1$ and $\log \beta_2$, for the addition of each nitrogenous base to (TPP)Mg were calculated spectrophotometrically by SQUAD. The measurements were made at 25.0 ± 0.5 °C on a Cary 14 Spectrometer with a 1.0-cm light path and a 5×10^{-5} M porphyrin solution. Ligand concentrations varied from 0 M to several molar, or in some cases neat liquid ligand was used as solvent. TBAP (0.1 M) was employed in the spectrophotometric measurements in order to insure conditions identical with those employed in our electrochemical investigations.[11] So that $\log \beta_1$ and $\log \beta_2$ could be accurately evaluated, the concentrations of ligand were grouped into lower and higher regions in the spectrophotometric titrations. For each ligand, 16 different spectra were obtained from 16 different titrations. Absorbances were taken between 555.0 and 630.0 nm at 5.0-nm intervals. With these absorbance data, estimations for $\log \beta_1$ and $\log \beta_2$ from a Benesi–Hildebrand plot were fed into SQUAD for processing.

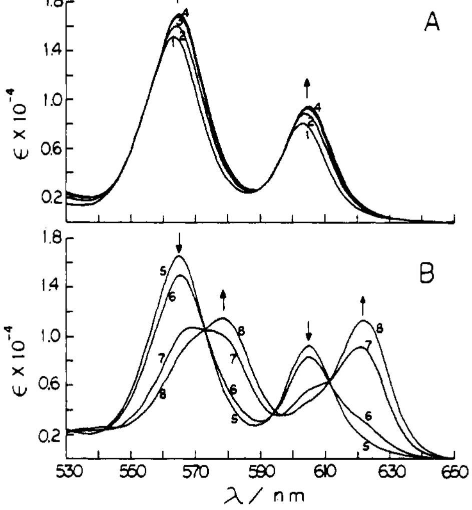

Figure 1. Optical absorption spectra obtained during spectrophotometric titration of 5×10^{-5} M (TPP)Mg, 0.1 M TBAP in CH_2Cl_2 with pyridine. The mole ratio of ligand to porphyrin is as follows. A: (1) 0:1; (2) 10:1; (3) 100:1; (4) 1000:1. B: (5) 4000:1; (6) 16000:1; (7) 120000:1; (8) 223000:1.

Results and Discussion

Eight optical absorption spectra in the spectrophotometric titration of (TPP)Mg with pyridine are shown in Figure 1. In the absence of coordinating ligand, the normal (TPP)Mg spectrum has a Soret band at λ_{max} 424 nm and two weaker visible bands at λ_{max} 603 and λ_{max} 563 nm, with a shoulder at λ_{max} 524 nm (only α and β bands are shown in Figure 1). Additions of a small amount of ligand to solutions containing 5×10^{-5} M(TPP)Mg in 0.1 M $TBAP/CH_2Cl_2$ produced red shifts in the optical absorption spectra. This spectral change is an indication of a new species formed: in this case, the monopyridinate complex. In similar studies (TPP)Zn was found to completely form the monopyridinate complex and dramatic spectral changes were observed when the pyridine concentration reached about 0.05 M.[1,12,13] Although (TPP)Mg has a comparable affinity for pyridine,[14] the observed spectral change is primarily in the intensity of absorption rather than in a band shift during the formation of ML according

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(6) Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443.

(7) Baum, S. J.; Burhan, B. F.; Plane, R. A. *Proc. Natl. Acad. Sci. U.S.A.* **1964**, *52*, 1439.

(8) Baum, S. J.; Plane, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 910.

(9) Timkovich, R.; Tulinsky, A. *J. Am. Chem. Soc.* **1969**, *91*, 4430.

(10) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals", 2nd ed.; Pergamon Press: Elmsford, NY, 1980.

(11) The redox measurements indicated a complicated oxidation mechanism in the presence of nitrogenous bases. This will be the subject of a later communication.

(12) Kadish, K. M.; Shiue, L. R.; Rhodes, R. K.; Bottomley, L. A. *Inorg. Chem.* **1981**, *20*, 1274.

(13) Nappa, M.; Valentine, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 5075.

(14) Lee, R. Y.; Hambright, P. *J. Inorg. Nucl. Chem.* **1970**, *32*, 477.

Table II. Absorption Maxima and Molar Absorptions for the α and β Bands of (TPP)Mg(L) and (TPP)Mg(L)$_2$

	λ_{max},[a] nm		$10^{-4}\epsilon$[b]			
			(TPP)Mg(L)		(TPP)Mg(L)$_2$	
ligand	α	β	α	β	α	β
1	614	569	0.38	1.35	1.40	1.17
2	616	573	0.36	1.07	1.20	1.24
3	619	575	0.20	0.86	1.37	1.30
4	619	577	0.22	0.68	1.28	1.30
5	621	578	0.17	0.66	1.40	1.34
6	621	578	0.18	0.69	1.44	1.30
7	622	579	0.15	0.58	1.26	1.26
8	622	579	0.14	0.60	1.57	1.45
9[c]	622	577	0.14	0.67	1.60	1.38
10[c]	623	577	0.13	0.66	1.61	1.53
11[c]	625	568	0.71	1.54	1.57	0.80
12[c]	629	566	0.03	1.63	1.17	0.66
13[c]	620	576	0.15	0.75	1.75	1.42
14	605	565	0.85	1.67	0.91	1.74
15	603	564	0.76	1.62	0.80	1.70
16	605	565	0.78	1.29	0.96	1.74
17	606	566	0.77	1.61	0.92	1.68
18	606	566	0.80	1.70	0.70	1.38

[a] Taken from the spectrum that corresponded to the highest ligand to porphyrin ratio in each spectrophotometric titration. [b] From SQUAD calculation results. [c] These complexes showed a split α and β band at the highest ligand concentration utilized.

to reaction 1 (Figure 1A). As seen from this figure, no isosbestic points are obtained on going from (TPP)Mg to (TPP)Mg(L). By comparison, the spectra in the region where the dipyridinate complex is the predominate species show a large bathochromic shift and clean isosbestic points (Figure 1B).

The results of SQUAD calculations are summarized in Table I. The 18 different ligands investigated are divided into three groups: non-sterically hindered ligands that cause an apparent spectral change (**1–13**), sterically hindered ligands (**14–16**), and non-sterically hindered ligands that cause little spectral change (**17**, **18**). Table II lists the peak maxima of the α and β bands at the highest ligand to porphyrin ratio in each spectrophotometric titration (e.g., spectrum 8 in Figure 1). In most cases, the magnitude of the red shifts were found to increase with the pK_a of the ligand.

So that the greatest conversion of ML to ML$_2$ could be obtained, the highest possible ligand concentrations were utilized (depending on solubility). It is clear that a change of solvent, from CH_2Cl_2/ligand mixtures to neat ligands as solvent, may cause nonspecific spectral changes in addition to those for complex formation. Data with and without the final spectrum that corresponded to the highest ligand to porphyrin ratio were processed separately and showed no significant difference between each other. Because of the small value of K_2, the use of very high ligand concentration was necessary. Calculations by SQUAD indicated that even with the highest ligand concentration, conversion of ML to ML$_2$ ranged only from 60% to 90%. Attempts to fit the model of ML and ML$_2$ to the data from spectrophotometric titrations lead to an overall fit to the data between 0.003 and 0.008, which is within experimental error. Other (unlikely) combinations of models (such as ML and M$_2$L$_3$) were tried and, as expected, did not fit the data. A combination of an acceptable deviation of the model fitting the absorbance data and an acceptable deviation of the calculated stability constants indicates that the reported log β_1 and log β_2 have a very high level of confidence. The only published stability constants for adding pyridine to (TPP)Mg (log K_1 = 3.3[1] and log K_2 = −0.75[2]) support this conclusion.

Plots of log K_1 and log K_2 vs. pK_a of each non-sterically hindered pyridine (**1–11**) are shown in Figure 2. As seen in this figure stability constants are linear functions of the ligand pK_a, with correlation coefficients of 0.9740 and 0.9391 for log K_1 and K_2, respectively. The increase of log K_1 with the ligand pK_a indicates that ligand to metal σ bonding dominates addition of the first ligand to the metal. This is consistent with an earlier study of (TPP)Zn(L) using the same group of ligands.[12] Ligands **14** and **15** (not shown in Figure 2) deviate from the line, probably because of steric hindrance effects for reaction 1. Imidazoles (**12**, **16**, and **17**) show a higher affinity for (TPP)Mg than do pyridines (and are also not shown in this plot). The increase in log K_1 and log K_2 (see Table I) is probably due to the net charge on Mg(II) resonating as

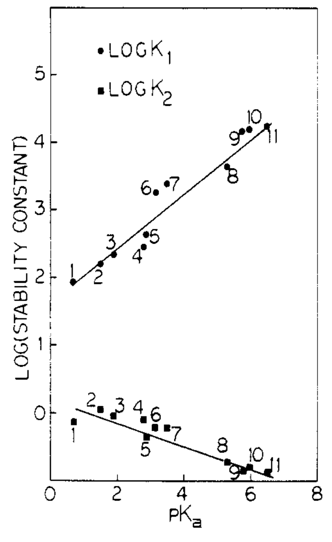
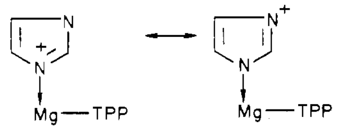


Figure 2. log (stability constant) vs. ligand pK_a.



The 1:1 adduct, ML, has square-pyrimidal geometry with the metal out of porphyrin plane.[15] Because the complexing of a second axial ligand is incompatible with retention of a nontrivial out-of-plane displacement of the metal, reaction 2 is less favorable as indicated by a smaller K_2.

It is interesting to note that log K_2 shows an inverse dependence of ligand basicity. This is consistent with earlier reported observations for a series of natural Mg(II) porphyrins complexed with nitrogenous bases.[2] Since Mg(II) has no d electrons, this trend is not due to the d–π bonding.

In a study of trimethylamine adducts with tin(II) halides, Hsu and Geanangel[16] reported that 1:2 adducts are less stable than the 1:1 adducts of the same acceptor. A similar effect is observed for the complexes in this study and is generally expected on electronic grounds. Through the donation of electron density by the first axial ligand, the positive charge on Mg(II) has been neutralized and Mg(II) then becomes a poor electron acceptor. This leads to electronegativity of the ligand as the deciding factor influencing the value of K_2 and the plot of log K_2 vs. pK_a of the ligand. The ligand of smaller pK_a has a larger electronegativity, thus a greater affinity for (TPP)Mg.

In summary, we have reported the first systematic study of ligand addition to Mg(II) porphyrins. Since the magnitude of the stability constants for ligand addition to neutral porphyrins is known to affect the redox properties of both the central metal[17] and the radical centered reaction,[12] these studies

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(15) Hoard, J. L. *Science (Washington, D.C.)* **1971**, 1295.
(16) Hsu, C. C.; Geanangel, R. A. *Inorg. Chem.* **1977**, *16*, 2529.

are of interest in terms of modifying redox behavior of metalloporphyrins by selective axial ligation. Spectroscopic and electrochemical studies are now in progress to determine if similar effects are obtained for other complexes of metalloporphyrins having closed d shells.

Acknowledgment. The authors wish to thank Dr. D. J. Leggett for the help in using his program SQUAD and Dr. W. W. Wendlandt for the TG measurements. Also the support of the National Science Foundation (Grant No. CHE-7921536) and the Robert A. Welch Foundation (Grant No. E-680) is gratefully acknowledged.

Registry No. (TPP)Mg(**1**)$_2$, 80186-45-4; (TPP)Mg(**2**)$_2$, 80186-46-5; (TPP)Mg(**3**)$_2$, 80186-47-6; (TPP)Mg(**4**)$_2$, 80206-17-3; (TPP)Mg(**5**)$_2$, 80186-48-7; (TPP)Mg(**6**)$_2$, 80186-49-8; (TPP)Mg(**7**)$_2$, 80186-50-1; (TPP)Mg(**8**)$_2$, 15672-67-0; (TPP)Mg(**9**)$_2$, 80186-51-2; (TPP)Mg(**10**)$_2$, 80186-52-3; (TPP)Mg(**11**)$_2$, 80186-53-4; (TPP)-Mg(**12**)$_2$, 80186-54-5; (TPP)Mg(**13**)$_2$, 80186-55-6; (TPP)Mg(**14**)$_2$, 80186-56-7; (TPP)Mg(**15**)$_2$, 80186-57-8; (TPP)Mg(**16**)$_2$, 80186-58-9; (TPP)Mg(**17**)$_2$, 80186-59-0; (TPP)Mg(**18**)$_2$, 80186-60-3.

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(17) Kadish, K. M.; Bottomley, L. A. *Inorg. Chem.* **1980**, *19*, 832.

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Molecular Structure and Quadratic Force Field of Chromyl Chloride, CrO_2Cl_2

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Received May 19, 1981

The molecular structure of chromyl chloride has been reinvestigated at room temperature by gas-phase electron diffraction. The analysis included corrections for the effects of vibrational averaging (shrinkage) calculated from an existing quadratic force field modified slightly by use of our structure to formulate the **G** matrix. Values for the symmetrized force constants are given. The structure results, which are based on and are consistent with C_{2v} symmetry for the molecule, are r_g(Cr=O) = 1.581 (2) Å, r_g(Cr–Cl) = 2.126 (2) Å, r_g(O···O) = 2.564 (8) Å, r_g(O···Cl) = 3.026 (4) Å, r_g(Cl···Cl) = 3.547 (7) Å, $\angle_\alpha$OCrO = 108.5 (4)°, $\angle_\alpha$ClCrCl = 113.3 (3)°, $\angle_\alpha$OCrCl = 108.7 (1) °, l(Cr=O) = 0.047 (2) Å, l(Cr–Cl) = 0.053 (2) Å, l(O···O) = 0.070 (8) Å, l(O···Cl) = 0.091 (4) Å, and l(Cl···Cl) = 0.105 (7) Å; parenthesized values are estimated 2σ. The calculated shrinkage corrections were tested. It was found that magnitudes about half those calculated gave slightly, but probably not significantly, better agreement with experiment.

Introduction

Valence-shell electron-pair repulsion (VSEPR) theory[2] has been widely used to predict and rationalize the structures of molecules and complex ions. The theory has enjoyed a particularly high degree of success when applied to compounds of the main-group elements, but it is somewhat less successful with compounds of the transition elements. For example, the structure of $TiCl_4$[3] is found to be tetrahedral in accordance with prediction, but $Nb(NMe_2)_5$[4] and WOF_4[5] are both square pyramidal instead of trigonal bipyramidal.

The metal atoms in these compounds are formally in the same oxidation state and have electron configuration d^0. Two other such compounds are the chromyl halides CrO_2F_2 and CrO_2Cl_2, the structures of which also do not agree with prediction from VSEPR theory. Thus both a recent electron-diffraction investigation[6] of CrO_2F_2 and an analysis[7] of its vibrational spectrum assigned a smaller value to the OCrO bond angle than to the FCrF angle, in contradiction to the VSEPR postulate that double bonds occupy more space on the coordination sphere than do single bonds. (An interpretation of the microwave spectrum[8] is in disagreement with this assignment, however.) Similarly, an early electron-diffraction study[9] of CrO_2Cl_2 revealed the OCrO angle to be smaller than the ClCrCl angle, but not by so much as in the fluorine compound.

The present study of chromyl chloride was stimulated by our desire to verify the above puzzling and unexpected result for the relative angle sizes. We also expected to improve the accuracy of the distance and angle measurements from the old study and to obtain values for the vibrational amplitudes.

Experimental Section

A commercial sample (Allied Chemical) of CrO_2Cl_2 was redistilled prior to use and a middle cut taken which was subsequently protected from daylight.

The diffraction experiments were performed in the OSU apparatus with the nozzle tip at room temperature and a sample-bath temperature of 2–5 °C. Other experimental conditions included an r^3 sector, 8 × 10 in. Kodak projector slide plates (medium contrast) developed for 10 min in D-19 developer diluted 1:1, 0.40–0.44-μA beam currents, 35–120-s exposure times, 0.05662–0.05665-Å electron wavelengths, and nozzle-to-plate distances of 752.77 and 296.78 mm. Data were obtained from four plates at each distance in the usual way,[10,11] and computer-generated backgrounds were subtracted.[12] The useful data covered the range $2.00 \leq s \leq 12.50$ Å^{-1} and $6.50 \leq s \leq 31.25$ Å^{-1} in intervals $\Delta s = 0.25$ Å^{-1} ($s = 4\pi\lambda^{-1} \sin(\theta/2)$; θ is the scattering angle). Curves of the levelled total intensity $s^4 I_T$ and the final

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(1) (a) University of Melbourne. (b) Oregon State University.

(2) Gillespie, R. J.; Nyholm, R. S. *Q. Rev., Chem. Soc.* **1957**, *11*, 339. Gillespie, R. J. "Molecular Geometry"; Van Nostrand-Reinhold: London, 1972.

(3) Morino, Y.; Vehara, H. *J. Chem. Phys.* **1966**, *45*, 4543.

(4) Heath, C.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1971**, 143.

(5) Robiette, A. G.; Hedberg, K.; Hedberg, L. *J. Mol. Struct.* **1977**, *37*, 105.

(6) Garner, C. D.; Mather, R.; Dove, M. F. A. *J. Chem. Soc., Chem. Commun.* **1973**, 633.

(7) Beattie, I. R.; Marsden, C. J.; Ogden, J. S. *J. Chem. Soc., Dalton Trans.* **1980**, 535.

(8) Graybeal, J. D.; Roe, D. W. *Proc. W. Va. Acad. Sci.* **1961**, *33*, 37.

(9) Palmer, K. J. *J. Am. Chem. Soc.* **1938**, *60*, 2360.

(10) Gunderson, G.; Hedberg, K. *J. Chem. Phys.* **1969**, *51*, 2500.

(11) Hagen, K.; Hedberg, K. *J. Am. Chem. Soc.* **1973**, *95*, 1003.

(12) Hedberg, L. "Abstracts", Fifth Austin Symposium on Gas-Phase Molecular Structure, Austin, Texas, March 1974, p 37.