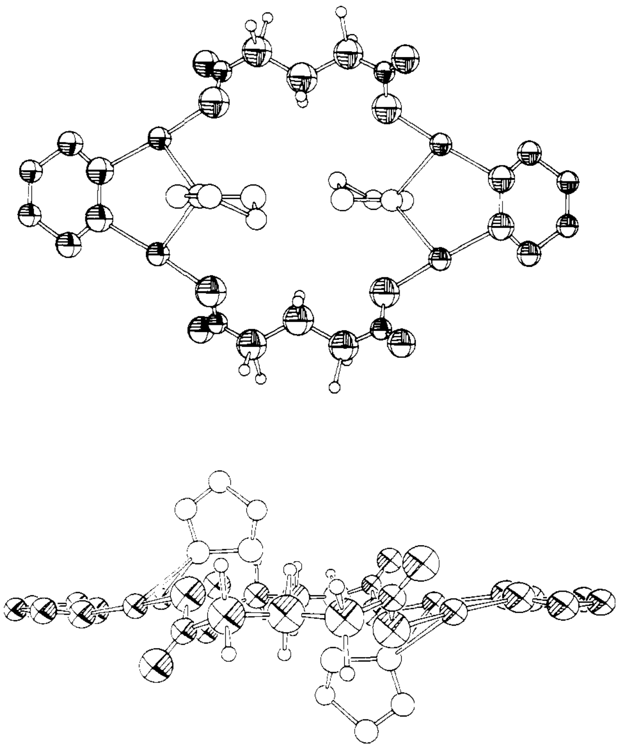


Figure 1. Two views of the structure of the 2:1 complex of perfluoroglutarate **8** with tetrahydrofuran. Fluorine atoms are represented by spheres of arbitrary size, and all hydrogen atoms are omitted for clarity.

An X-ray crystallographic study of this complex has revealed that its unit cell contains the 2:1 structure shown in Figure 1 and a second, closely related 6:1 motif.[5] In both complexes, the macrocyclic 22-membered ring of perfluoroglutarate **8** is approximately planar and surrounds a hole nearly 12 Å long and 7 Å wide. In the 2:1 complex, the oxygen atom of each THF molecule interacts symmetrically with the mercury atoms of a 1,2-phenylenedimercury unit, and one THF is bound above the plane of the macrocyclic ring while the other lies below. In the 6:1 complex, two molecules of THF are bound above the macrocyclic ring by similar interactions and two are bound below. The additional molecules of THF interact outside the ring with individual atoms of mercury. Both structures obey two rules generally followed by complexes of Hg(II): mercury forms two strong collinear primary bonds, and it retains appreciable acidity in the plane perpendicular to these primary bonds, allowing secondary coordination. Thus the endocyclic C–Hg–O angle in the 2:1 complex is 174 (2)°, and the C–Hg–O angle involving the oxygen atom of THF is 100 (2)°. Other angles and distances are similar to those found in related derivatives of 1,2-phenylenedimercury[1] and in phenylmercuric trifluoroacetate.[6]

Of special importance is the distance from mercury to the coordinated oxygen of THF, which is 2.85 (4) Å in the 2:1 complex. Since the van der Waals radii of oxygen and mercury are approximately 1.4 and 1.5–1.73 Å,[7,8] respectively, the mercury–oxygen interactions in the complexes are moderately strong. As a result, the bound molecules of THF resist elimination during drying at 25 °C/0.1 Torr. Nevertheless, all are displaced when a better Lewis base like bidentate dimethoxyethane is added. The particular orientation of the four strongly electrophilic sites in perfluoroglutarate **8** should make it ideal for the recognition and selective binding of molecules containing two basic sites separated by about 7 Å.

The remarkably efficient formation of the large ring of perfluoroglutarate **8** is a consequence of the rigidity of the 1,2-phenylenedimercury units, the collinearity of primary bonds to mercury, and the favorable dimensions and conformation of perfluoroglutarate bridges. Perfluorosuccinate bridges may be too short to allow a similar macrocyclization, and the antiperiplanar orientation of carboxylate groups normally preferred by perfluorosuccinates may be an additional disadvantage.[9]

Constructing macrocyclic multidentate Lewis acids by using perfluorodicarboxylate bridges to link strongly electrophilic sites is a simple, powerful, and potentially general strategy. Study of the structure and coordination chemistry of these macrocyclic multidentate Lewis acids should be richly rewarding.

Acknowledgment. This work was financially supported by the Natural Sciences and Engineering Research Council of Canada and the Ministère de l'Éducation du Québec. We thank Robert Mayer for recording our ^{199}Hg NMR spectra.

Supplementary Material Available: Spectroscopic and analytical data for the THF complex of perfluoroglutarate **8**, description of the crystal structure, and tables of bond distances and angles and of atomic positional and thermal parameters (12 pages). Ordering information is given on any current masthead page.

---

(4) The structure assigned to this complex is consistent with its elemental analysis and its IR, ^{1}H NMR, and ^{199}Hg NMR spectra. These data are included in the supplementary material.

(5) (a) Beauchamp, A. L.; Simard, M., unpublished work. (b) Crystals of the THF complex of perfluoroglutarate **8** belong to the orthorhombic space group *Pnnm*, with a = 12.261 (9) Å, b = 24.116 (14) Å, c = 16.954 (2) Å, and V = 5013.1 Å^3. An Enraf-Nonius CAD-4 diffractometer was used to collect a set of intensity data ($2\theta \leq 50.0°$, Mo Kα, 1387 non-zero reflections). The structure was solved by Patterson and difference Fourier synthesis and refined by full-matrix least-squares calculations to R = 0.088, R_w = 0.095, and goodness-of-fit ratio = 2.61. The atomic positional and thermal parameters are included in the supplementary material.

(6) Kamenar, B.; Penavić, M.; Hergold-Brundić, A. *Croat. Chem. Acta* **1984**, *57*, 145–152.

(7) Kuz'mina, L. G.; Bokii, N. G.; Struchkov, Yu. T. *Usp. Khim.* **1975**, *44*, 134–155. Grdenić, D. *Q. Rev., Chem. Soc.* **1965**, *19*, 303–328.

(8) For references, see: Wardell, J. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 2, pp 863–978.

(9) Karipides, A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 1659–1662.

Formation, Chemistry, and Thermochemistry of Primary Amide Complexes of Fe$^+$ and Co$^+$ in the Gas Phase

Steven W. Buckner and Ben S. Freiser*

Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Received March 4, 1987

Recently there has been renewed interest in the preparation and properties of transition-metal–amide complexes.[1,2] Later transition-metal amides may have catalytic utility in the synthesis of amines and other nitrogen-containing organic compounds[3] but to date very few have been reported. The instability of these complexes has been attributed to the unfavorable d $\leftarrow$ p interaction for later transition metals.[1a] Because of this, the majority of the amide complexes reported have contained α-nitrogen groups such as SiR$_3$ which can withdraw pπ electron density from the nitrogen and thus stabilize the M–N bond.

---

(1) For a discussion of transition-metal–amide complexes, see: Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C.; *Metal and Metalloid Amides*; Ellis Horwood Limited: West Sussex, England, 1980.

(2) (a) Cetinyaka, B.; Lappert, M. F.; Torroni, S. *J. Chem. Soc., Chem. Commun.* **1979**, *843*. (b) Lay, P. A.; Sargeson, A. M.; Skeleton, B. W.; White, A. H. *J. Am. Chem. Soc.* **1981**, *104*, 6161. (c) Anderson, R. A.; Mainz, V. V. *Organometallics* **1984**, *3*, 675. (d) Bryndza, H. E.; Fultz, W. C.; Tam, W. *Organometallics* **1985**, *4*, 1145. (e) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *Organometallics* **1985**, *4*, 939. (f) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *Organometallics* **1986**, *4*, 2469.

(3) (a) Yamamoto, Y.; Yatagai, H.;, Murayama, K. *J. Chem. Soc., Chem. Commun.* **1980**, *835*. (b) Hedden, D.; Roundhill, D. M.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 5014.

0002-7863/87/1509-4715$01.50/0

Primary amide complexes are extremely rare and with few exceptions have involved early transition metals. A recent gas-phase study provided evidence that $D°(Co^+-NH_2)$ could be less than 19 kcal/mol.[4,5] We report here on the formation of iron and cobalt primary amide complexes in the gas phase and on their chemistry and thermochemistry which, to the contrary, indicates relatively strong metal–amide bonding.

Experiments were performed on two instruments, a prototype Nicolet FTMS-1000 equipped with a 5.2-cm cubic-trapping cell situated between the poles of a Varian 15-in. electromagnet maintained at 0.9 T and a Nicolet FTMS-2000 dual cell instrument maintained at 3.0 T.[6,7] Laser desorption was used to generate Co^+ and Fe^+ from pure foils of the appropriate metal.[8] MOH^+ and M(cyclopentadiene)$^+$ were produced via reactions 1[9] and 2,[10] respectively. Cyclopentane and nitromethane reagents were introduced into the cell via a pulsed valve[11] to avoid complicating secondary reactions. NH_3 was introduced into the cell ~400 ms later via a second pulsed valve. Double resonance ejection experiments were used to isolate ML^+ for reaction with NH_3 and to isolate MNH_2^+ for subsequent reactions.[12] Argon was used as the collision gas for collision-induced dissociation (CID) experiments[13] at a pressure of $\sim 1 \times 10^{-5}$ Torr. Argon also served to collisionally cool MOH^+ and $M(c\text{-}C_5H_6)^+$, with ~100–150 collisions occurring prior to reaction with NH_3.[14]

$$M^+ + CH_3NO_2 \rightarrow MOH^+ + CH_2NO \qquad (1)$$

$$M^+ + c\text{-}C_5H_{10} \rightarrow M(c\text{-}C_5H_6)^+ + 2H_2 \qquad (2)$$

$$(M = Co, Fe)$$

$CoOH^+$ and $FeOH^+$ react with NH_3 by reaction 3. From $D°(Co^+-OH) = 71 \pm 3$ kcal/mol and $D°(Fe^+-OH) = 73 \pm 3$ kcal/mol, reported previously,[15] reaction 3 implies $D°(Co^+-NH_2) > 56 \pm 3$ kcal/mol and $D°(Fe^+-NH_2) > 58 \pm 3$ kcal/mol.[16] $CoNH_2^+$ reacts with benzene via displacement of $NH_2^•$ to form Co(benzene)$^+$, but it is unreactive with acetonitrile, indicating 68 ± 5 kcal/mol $= D°(Co^+-\text{benzene})$[17] $> D°(Co^+-NH_2) > D°(Co^+-CH_3CN) > 61 \pm 4$ kcal/mol.[18] Thus, we assign $D°(Co^+-NH_2) = 65 \pm 8$ kcal/mol. $NH_2^•$ is not displaced from $FeNH_2^+$ by benzene, indicating $D°(Fe^+-NH_2) > D°(Fe^+-\text{benzene}) = 55 \pm 5$ kcal/mol,[17] which is consistent with $D°(Fe^+-NH_2) > 58 \pm 3$ kcal/mol obtained from reaction 3.

$$MOH^+ + NH_3 \rightarrow MNH_2^+ + H_2O \qquad (3)$$

$$(M = Co, Fe)$$

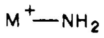
Both $CoNH_2^+$ and $FeNH_2^+$ react with propene and cyclopropane, reactions 4 and 5, to generate presumably metal–allyl species. Reaction 4 implies $D°(Fe^+-NH_2) < 72 \pm 7$ kcal/mol, from $D°(Fe^+-\text{allyl}) = 56 \pm 7$ kcal/mol reported previously.[19] Reactions 3 and 4 indicate 72 ± 7 kcal/mol $> D°(Fe^+-NH_2) > 58 \pm 3$ kcal/mol from which we assign $D°(Fe^+-NH_2) = 67 \pm 12$ kcal/mol. Reaction 4 also implies $D°(Co^+-\text{allyl}) > 50 \pm 7$ kcal/mol, which is in accord with a previously reported value of $D°(Co^+-\text{allyl}) > 74$ kcal/mol.[20]

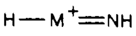
$$MNH_2^+ + \text{propene} \rightarrow M^+(\text{allyl}) + NH_3 \qquad (4)$$

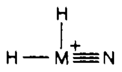
$$MNH_2^+ + \text{cyclopropane} \rightarrow M^+(\text{allyl}) + NH_3 \qquad (5)$$

$$(M = Co, Fe)$$

The MNH_2^+ ions may consist of a metal amide (I), a metal hydride nitrene (II), or a metal dihydride nitride (III). Both $FeNH_2^+$ and $CoNH_2^+$ undergo CID via direct cleavage to form M^+, exclusively, at all energies studied (0–100 eV) indicating I as the structure since loss of $H^•$ and/or H_2 would have been expected as products from II and III. Displacement of $NH_2^•$ from $CoNH_2^+$ by benzene and the absence of $H^•$ and/or H_2 displacement also suggest structure I. MNH_2^+ (M = Co, Fe) does not undergo H/D exchange with D_2, C_2D_4, or propene-d_6,[21] but it does react with propene-d_6 to produce the metal-perdeuterioallyl cation and NH_2D, reaction 6, exclusively. Absence of H/D exchange is again consistent with structure I. Finally, $FeNH^+$, formed in reaction 7, reacts with benzene by reaction 8. The analogous reaction is not observed with MNH_2^+ further indicating II is probably not the structure. Reactions 7 and 8 imply a value of 81 kcal/mol $> D°(FeNH^+) > 41$ kcal/mol, obtained from $D°(Fe^+-O) = 68 \pm 3$ kcal/mol[22] and assuming that aniline parent cation is the product in reaction 8.


I


II

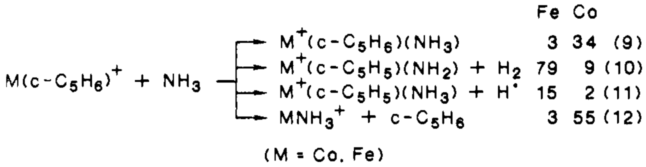

III

$$MNH_2^+ + \text{propene-}d_6 \rightarrow MC_3D_5^+ + NH_2D \qquad (6)$$

$$FeO^+ + NH_3 \rightarrow FeNH^+ + H_2O \qquad (7)$$

$$FeNH^+ + \text{benzene} \rightarrow C_6H_7N^+ + Fe \qquad (8)$$

Interestingly, $M\text{-}c\text{-}C_5H_6^+$ (M = Co, Fe) reacts with NH_3 by reactions 9–12. Collisional activation of what is presumably $Fe(c\text{-}C_5H_5)(NH_2)^+$, generated in reaction 10, yields loss of NH (15%) and NH_2 (85%) at low energies (0–20 eV lab) and loss of NH_2 (41%), $c\text{-}C_5H_5$ (10%), NH (30%), and both ligands (19%) at higher energies (20–100 eV lab).



The gas-phase thermochemical results presented here for $FeNH_2^+$ and $CoNH_2^+$ indicate that, contrary to previous belief, these species do not have intrinsically weak M^+-NH_2 bonds. A variety of metal–amide complexes are currently under further chemical and photochemical investigation in our laboratory.

Acknowledgement is made to the Division of Chemical Sciences, Office of Basic Energy Sciences, United States Department of Energy (DE-AC02-80ER10689) for supporting the transition-metal ion research and to the National Science Foundation (CHE-8310039) for the continued support of the Fourier transform mass spectrometry instrumentation. S.W.B. gratefully acknowledges the Purdue Research Foundation for providing fellowship support. The authors also acknowledge I. P. Rothwell and D. Swanson for helpful discussions.

---

(4) (a) Allison, J.; Radecki, B. D. *J. Am. Chem. Soc.* **1984**, *106*, 946. (b) Babinec, S. J.; Allison, J. *J. Am. Chem. Soc.* **1984**, *106*, 7718.

(5) For a review of gas-phase metal-ion chemistry, see: Allison, J. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley-Interscience: New York, 1986; Vol. 34, p 628.

(6) Comisarow, M. B.; Marshall, A. G. *Chem. Phys. Lett.* **1974**, *26*, 489.

(7) Many of the experiments reported here were performed on both instruments, and the same results were obtained.

(8) Cody, R. B.; Burnier, R. C.; Reents, W. D., Jr.; Carlin, T. J.; McCrery, D. A.; Lengal, R. K.; Freiser, B. S. *Int. J. Mass Spec. Ion Phys.* **1980**, *33*, 37.

(9) Cassady, C. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*; 1573.

(10) Armentrout, P. B., Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6628.

(11) Carlin. T. J.; Freiser, B. S. *Anal. Chem.* **1983**, *55*, 571.

(12) Comisarow, M. B.; Parisod, G.; Grassi, V. *Chem. Phys. Lett.* **1978**, *57*, 413.

(13) Cody, R. B.; Freiser, B. S. *Int. J. Mass Spec. Ion Phys.* **1982**, *41*, 199.

(14) Ahmed, M. S.; Dunbar, R. C. *J. Am. Chem. Soc.* **1987**, *109*, 3215.

(15) Cassady, C. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 6176.

(16) Supplementary thermochemical information taken from the following: Rosenstock, H. M.; Draxl, D.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data Suppl. 1* **1977**, *6*.

(17) Hettich, R. L.; Jackson, T. C.; Stanko, E. M.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 5086.

(18) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 4623.

(19) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7484.

(20) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 3891.

(21) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 72.

(22) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784.