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A Hydrogen-Bonded Chain Involving both N–H···N and N–H···Co Hydrogen Bonds. Low-Temperature X-ray Crystal Structure of $[(NMP)_3H_2][Co(CO)_4]_2$ (NMP = *N*-Methylpiperazine)

Lee Brammer* and Dong Zhao

Department of Chemistry, University of Missouri—St. Louis, 8001 Natural Bridge Road, St. Louis, Missouri 63121-4499

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Summary: $[(NMP)_3H_2][Co(CO)_4]_2$ *(1; NMP = N-methylpiperazine) is the first example of a compound which exhibits both conventional hydrogen bonding, in which a proton lies between two electronegative nonmetal centers, and hydrogen bonding involving an electron-rich metal center. In this case N–H···N and N–H···Co hydrogen bonds give rise to a five-component hydrogen-bonded chain. Furthermore, two secondary ammonium centers (N(11) and N(31)) simultaneously function as hydrogen-bond donors to an amine center and to a* d^{10} *cobalt center. The crystal structure of 1 has been determined at 135(5) K by X-ray diffraction.*

Hydrogen bonding is a topic which has attracted a great deal of interest for many years,[1] particularly in the realms of organic chemistry and biological chemistry.[1e] Typically, hydrogen bonds have been considered to be confined to the interaction of non-metals (X1) that have lone pairs of electrons, such as nitrogen, oxygen, sulfur, or halogens, with hydrogen atoms which are covalently bound to one of these same electronegative elements (or to carbon[1f]) (X2). This accounts for the predominant electrostatic component of these $X2^{\delta-}–H^{\delta+}···X1^{\delta-}$ interactions, particularly when X1 is an anionic species. Such conclusions are borne out in many theoretical studies.[2]

More recently, transition-metal-containing examples of interactions that are analogous to conventional hydrogen bonds have been reported.[3,4] These involve an electron-rich transition metal as the hydrogen-bond acceptor. Such interactions are, therefore, best described as three-center–four-electron (3c–4e) interactions, and the use of structural and spectroscopic criteria to distinguish these interactions from the more well-known (3c–2e) agostic interactions has been discussed.[3a]

We have previously described salts of the form $R_3NH^+Co(CO)_4^-$, prepared from reaction of R_3N and $HCo(CO)_4$, which involve N–H···Co hydrogen bonds.[3b,c] Furthermore, we have shown that use of a di(tertiary amine) can lead to N–H···N hydrogen-bonded products as well as those forming N–H···Co interactions.[3c] Here we report the structure of a compound which exhibits both N–H···N and N–H···Co hydrogen bonds, obtained by use of a diamine which has both a tertiary and a secondary amine function.

Reaction of $HCo(CO)_4$ with 5 equiv of *N*-methylpiperazine under conditions previously described[5] for the preparation of the salts $R_3NH^+Co(CO)_4^-$ (R = Me, Et) and $(DABCO)H^+Co(CO)_4^-$ (DABCO = 1,4-diazabicyclo[2.2.2]octane) yields the remarkable hydrogen-bonded product $[(NMP)_3H_2][Co(CO)_4]_2$ (1; NMP = *N*-methylpiperazine), which involves both N–H···N and N–H···Co hydrogen bonds. 1 is a five-component "chain" comprising three diamine units linked by N–H···N hydrogen bonds, capped at each end by $Co(CO)_4^-$ anions which interact via N–H···Co hydrogen bonds. This is the first example of a hydrogen-bonded chain involving both conventional hydrogen bonding (i.e. N–H···N) and hydrogen bonds to metal centers. Furthermore, two secondary ammonium nitrogen centers (N(11) and N(31)) simultaneously function as hydrogen bond donors to an amine nitrogen and to a d^{10} cobalt center.

Colorless air-sensitive crystals suitable for X-ray diffraction were obtained[6] from the reaction mixture after

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(1) (a) Schuster, P., Zundel, G., Sandorfy, C., Eds. *The Hydrogen Bond*; North-Holland: Amsterdam, New York, Oxford, 1976. (b) Hamilton, W. C.; Ibers, J. A. *Hydrogen Bonding in Solids*; W. A. Benjamin: New York, 1968. (c) Pimental, G. C.; McClellan, A. L. *The Hydrogen Bond*; W. H. Freeman: San Francisco, 1960. (d) Hadzi, D., Ed.; *Hydrogen Bonding*; Pergamon: New York, 1959. (e) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer-Verlag: Berlin, 1991. (f) Green, R. D. *Hydrogen Bonding to C-H Groups*; Wiley-Interscience: New York, 1974.

(2) For reviews of ab initio theoretical studies of hydrogen bonding involving ions, see: Deakyne, C. A. *In Molecular Structure and Energetics*; VCH: New York, 1987; Vol. 4, Chapter 4, and references therein.

(3) (a) Brammer, L.; Charnock, J. M.; Goggin, P. L.; Goodfellow, R. J.; Orpen, A. G.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1991**, 1789. (b) Brammer, L.; McCann, M. C.; Bullock, R. M.; McMullan, R. K.; Sherwood, P. *Organometallics* **1992**, *11*, 2339. (c) Brammer, L.; Zhao, D.; Ladipo, F. T. *J. Am. Chem. Soc.*, submitted for publication.

(4) (a) Wehman-Ooyevaar, I. C. M.; Grove, D. M.; Kooijman, H.; van der Sluis, P.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1992**, *114*, 9916. (b) Wehman-Ooyevaar, I. C. M.; Grove, D. M.; de Vaal, P.; Dedieu, A.; van Koten, G. *Inorg. Chem.* **1992**, *31*, 5484. (c) Kazarian, S. G.; Hamley, P. A.; Poliakoff, M. *J. Am. Chem. Soc.* **1993**, *115*, 9069.

(5) $HCo(CO)_4$ was prepared from $Co_2(CO)_8$ by literature methods,[5b] using dimethylformamide rather than pyridine to disproportionate the dimer, and added to the diamine by vacuum transfer. The product 1 was formed on warming from −196 °C and drying under vacuum. Similar procedures have been reported for the synthesis of $R_3NH^+Co(CO)_4^-$ (R = Me, Et)[5c] and $(DABCO)H^+Co(CO)_4^-$.[3c] (b) Sternberg, H. W.; Wender, I.; Friedel, R. A.; Orchin, M. *J. Am. Chem. Soc.* **1953**, *75*, 2717. (c) Calderazzo, F.; Fachinetti, G.; Marchetti, F.; Zanazzi, P. F. *J. Chem. Soc., Chem. Commun.* 1981, 181.

(6) (a) Crystal data for 1: $C_{23}H_{37}N_6O_8Co_2$, monoclinic, *C*2/*c* (No. 15), $a = 40.210(11)$ Å, $b = 8.232(2)$ Å, $c = 18.648(6)$ Å, $\beta = 100.42(2)°$, $V = 6071(3)$ Å^3, $Z = 8$, $D_c = 1.408$ g cm^{-3}, $T = 135(5)$ K, μ(Mo Kα) = 1.144 mm^{-1}. Data were collected on a Siemens R3m/V diffractometer using $\omega–2\theta$ scans ($2\theta_{max} = 51.5°$); of the 6190 reflections measured, 5678 were unique ($R_{int} = 0.067$) and 2496 with $F > 4.0\sigma(F)$ were used in least-squares refinement. The structure was solved by direct methods and refined to $R(F) = 0.078$, $R_w(F) = 0.080$, and $S(F) = 1.102$. All non-H atoms were refined anisotropically; hydrogen atoms were assigned fixed displacement parameters ($U_{iso} = 0.05$ Å^2). All methylene hydrogen atoms, together with H(11b) and H(31b), were assigned idealized positions, the positional parameters of H(11a), H(21a), and H(31a) were refined freely. Systematic error associated with the carbonyl carbon atoms C(103), C(104), and C(203) is evident upon examination of the U_{ij} values. Efforts to examine absorption and extinction as sources for this error were unsuccessful. Distances and angles associated with these atoms should, therefore, be considered as less accurate than other interatomic dimensions. All crystallographic calculations were performed using the SHELXTL suite of programs.[6b] (b) Sheldrick, G. SHELXTL 4.2; Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1991.

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Table 1. Comparison of the Geometries of Salts with N–H···Co Hydrogen Bonds with That of $HCo(CO)_4$

compd	N···Co (Å)	C_{eq}–Co–C_{eq} (deg)	C_{ax}–Co–C_{eq} (deg)	temp (K)	X/N/E[a]	ref
$Et_3NH^+Co(CO)_4^-$	3.684(2)	112.4(1)	106.3(1)	123.0(5)	N	7
$Me_3NH^+Co(CO)_4^-$	3.402(4)	112.7(14)	105.9(11)	295	X[b]	5c
$(DABCO)H^+Co(CO)_4^-$	3.437(3)	111.2(2)	107.2(2)	135(5)	X[b]	3c
$[(NMP)_3H_2][Co(CO)_4]_2$	3.639(1)	112.1(9)	106.7(7)	135(5)	X[b]	c
$HCo(CO)_4$	na[d]	117.3	99.7(6)	238	E	9

[a] X = X-ray diffraction, N = neutron diffraction, E = electron diffraction. [b] Averaged dimensions, with esd's (in parentheses) calculated according to $[\sum(d_i - d)^2/n(n-1)]^{1/2}$. [c] This work. [d] na = not applicable.

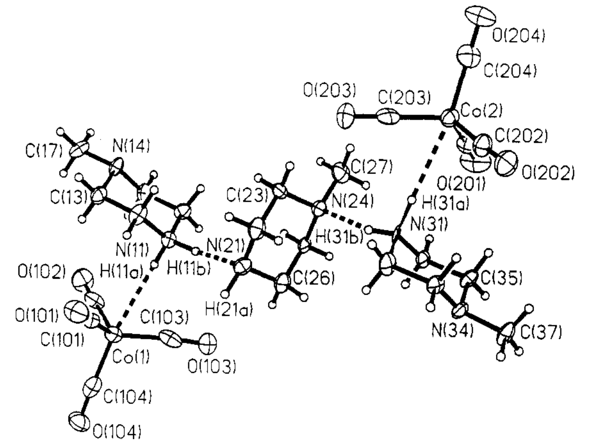

Figure 1. Molecular structure of 1 shown with 50% probability ellipsoids for all non-hydrogen atoms. Selected distances (Å): N(11)···Co(1), 3.638(9); N(11)–H(11a), 1.05(8); Co(1)···H(11a), 2.63(9); N(31)···Co(2), 3.639(9); N(31)–H(31a), 0.97(9); Co(2)···H(31a), 2.67(8); N(11)···N(21), 2.83(1); N(24)···N(31), 2.80(1). Selected angles (deg): N(11)–H(11a)···Co(1), 161(8); N(31)–H(31a)···Co(2), 176(9); C(101)–Co(1)–C(102), 111.6(6); C(101)–Co(1)–C(103), 110.1(6); C(102)–Co(1)–C(103), 115.2(6); C(101)–Co(1)–C(104), 104.8(6); C(102)–Co(1)–C(104), 107.1(6); C(103)–Co(1)–C(104), 107.5(6); C(201)–Co(2)–C(202), 110.3(6); C(201)–Co(2)–C(203), 114.9(6); C(202)–Co(2)–C(203), 110.5(6); C(201)–Co(2)–C(204), 105.2(6); C(202)–Co(2)–C(204), 109.6(6); C(203)–Co(2)–C(204), 106.0(6).

removal of hexane solvent and excess *N*-methylpiperazine at reduced pressure on a Schlenk line. The structure of 1 is shown in Figure 1. As in the previous $R_3NH^+Co(CO)_4^-$ salts which have been characterized crystallographically,[3b,c,5c] the three "equatorial" carbonyl groups, which comprise the "face" of the $Co(CO)_4^-$ anions at which the N–H···Co interactions occur, bend away from the N–H group toward the "axial" carbonyl ligand (Table 1). However, it appears that there is no correlation between the N···Co separation, presumably a measure of the strength of the N–H···Co interaction, and the extent to which the carbonyl groups bend back, at least within the range of salts studied to date. Nevertheless, it is clear that averaged $Co(CO)_4$ geometries of each of these salts are intermediate between that of a free (T_d) $Co(CO)_4^-$ anion and that of its conjugate acid $HCo(CO)_4$.

Although the structure of 1 shows an *averaged* anion geometry very similar to that of $Et_3NH^+Co(CO)_4^-$, unlike that of $Et_3NH^+Co(CO)_4^-$ the distortion away from T_d symmetry of the metal coordination geometry resulting from the N–H···Co interaction is not toward C_{3v} symmetry but is closer to C_s symmetry.[8] The N–H···C(O) separations

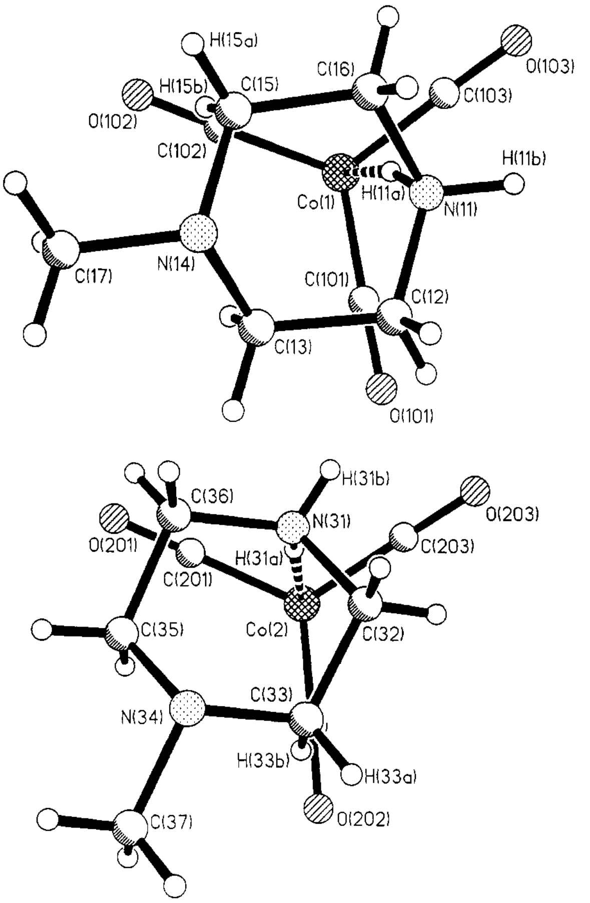

Figure 2. Views approximately parallel to (a, top) the Co(1)–C(104) vector and (b, bottom) the Co(2)–C(204) vector illustrating the two N–H···Co hydrogen bonds and the asymmetric environment of the $Co(CO)_4^-$ anions presented by the secondary ammonium cations.

(H(11a)···C(101) = 2.64(11) Å, H(11a)···C(102) = 3.00(9) Å, H(11a)···C(103) = 2.52(7) Å; H(31a)···C(201) = 2.51(11) Å, H(31a)···C(202) = 3.12(9) Å, H(31a)···C(203) = 2.62(7) Å) also indicate that the approach of the N–H group to the $Co(CO)_4^-$ anion is not directly towards the center of one CoC_3 face but rather lies between this trajectory and one directed toward a CoC_2 edge, as illustrated in Figure 2. These differences between 1 and $Et_3NH^+Co(CO)_4^-$ lie primarily in the fact that in 1 a secondary ammonium group, rather than a more symmetrical tertiary ammonium group, interacts with the metal center. The hydrogen substitutents (H(11b) and H(31b)) at the ammonium centers should be less sterically demanding than the additional alkyl substituents present in the previous studies involving tertiary ammonium ions.

The two N–H···N hydrogen bonds are presumed to be asymmetric on the basis of their N···N separations[10] (N(11)···N(21) = 2.83(1) Å, N(24)···N(31) = 2.80(1)Å) and

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(7) (a) The structure of $Et_3NH^+Co(CO)_4^-$ has been determined by neutron diffraction at temperatures of 123,[3c] 60,[7b] and 15 K.[3b] (b) Brammer, L.; McCann, M. C.; Bullock, R. M.; McMullan, R. K.; Sherwood, P. Unpublished work.

(8) This is apparent from examination of the C–Co–C angles. Approximate planes of symmetry for the two $Co(CO)_4^-$ anions are defined by C(101)–Co(1)–C(104) and C(201)–Co(2)–C(204).

(9) McNeill, E. A.; Scholer, F. R. *J. Am. Chem. Soc.* **1977**, *99*, 6243.

are the first example of hydrogen bonding between piperazine moieties to be characterized crystallographically.

In summary, we have prepared and characterized by low-temperature X-ray crystallography the first example of a compound in which an ammonium center simultaneously acts as a hydrogen-bond donor to a non-metal (amine) center and to a metal center. The compound, $[(NMP)_3H_2][Co(CO)_4]_2$, exists as an unusual five-unit hydrogen-bonded chain of three diamines and two carbonyl-ligated cobalt centers. Efforts are underway to examine the possibility of producing longer hydrogen-bonded chains and networks in which hydrogen bonding to the metal center does not terminate the chain.

Acknowledgment. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and from the University of Missouri Research Board, Weldon Springs and Research Incentive Award funds, is gratefully acknowledged.

Supplementary Material Available: Tables of crystallographic data, positional and displacement parameters, and interatomic distances and angles for 1 (9 pages). Ordering information is given on any current masthead page.

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(10) Symmetrical N–H–N hydrogen bonds are associated with shorter N···N separations on the order of 2.6 Å. For example, see: Roziere, J.; Belin, C.; Lehmann, J. *J. Chem. Soc., Chem. Commun.* **1982**, 388. Glidewell, C.; Holden, H. D. *Acta Crystallogr.* **1982**, *B38*, 667. Hydrogen atoms H(11b) and H(31b) were included in calculated positions in the final refinement model for 1.