Synthesis, Crystal Structure, and Spectroscopic and Magnetic Properties of a New [$Co_4O(OOCNC_9H_{18})_6$] Cluster

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*Summary: The synthesis, X-ray structure, and NMR (^1H, ^{13}C, ^{17}O) and magnetic characterization of the complexes [$Co(CO)_2(tmpo)$] (**1**) and [$Co_4O(OOCNC_9H_{18})_6$] (**2**) are reported. Reaction of $Co_2(CO)_8$ in the presence of a 4-fold excess of tmpo yields in a few minutes the blue carbamato complex **2** in >80% yield. The reaction possibly takes place by a cascade mechanism with the complex [$Co(CO)_2tmpo$] (**1**) as an intermediate and the nitroxyl radical acting as an oxidizing agent.*

Introduction

The nitroxyl radical 2,2,6,6-tetramethylpiperidin-1-oxyl (tmpo) has been successfully used (a) in the design of new organic magnetic materials,[1] (b) as a paramagnetic ligand to study magnetic interactions of organic radicals with metal ions,[2] and (c) as a building block in the preparation of new π-extended organic donor molecules exhibiting conducting and magnetic properties.[3] We have also shown that tmpo is a valuable spin scavenger of metal carbonyl radicals.[4] For instance, photolysis of $Co_2(CO)_8$ promotes the fission of the Co−Co bond, generating the radical $Co(CO)_4^\bullet$, which reacts with an equimolar amount of the tmpo group to yield [$Co(CO)_2(tmpo)$] (**1**).[4b] The molecular structure of complex **1** was determined by single-crystal X-ray diffraction, showing that the Co^I atom is in a planar coordination with the two carbonyls and the O−N group of the tmpo ligand. No addition of CO, PR_3, or H_2 to **1** could be effected, since the two methyl groups of the coordinated tmpo protect the Co atom from the upper and lower side of the planar molecular arrangement.

In this paper we report the synthesis and spectroscopic and magnetic characterization of the new cluster [$Co_4(\mu_4\text{-}O)(OOCNC_9H_{18})_6$] (**2**).[5] Surprisingly, reaction of [$Co_2(CO)_8$] with a 4-fold excess of tmpo promoted the generation of the blue carbamato complex **2** in a few minutes. Even though the mechanism of formation of this complex is not completely understood, this synthetic methodology opens a new route to clusters of the type [$M_4(\mu_4\text{-}O)$]$^{6+}$. Such clusters, with a four-coordinate oxygen atom occupying the center of a tetrahedron of divalent metal ions, is a classic structure in inorganic chemistry.[6] The first such complexes reported were the acetate derivatives ([$M_4O(Ac)_6$]) of beryllium[7] and zinc.[8] Later, similar complexes of Zn,[9] Mn,[10] Fe,[10] and Cr,[11] in which the acetate groups are replaced by other bridging ligands, were prepared.

In the case of cobalt, the first cluster with a [$M_4(\mu_4\text{-}O)$]$^{6+}$ core was obtained in 1966 by pyrolysis of anhydrous cobalt pivalate under vacuum.[12] Since then, only a few more complexes, [$\{Ir(aet)_3\}_4Co_4O]Br_6$][13] (where aet = 2-aminoethanethiolate), [$Co_4O(O_2CCCo_3(CO)_9)_6$],[14] and, recently, [$Co_4O(DPhF)_6$][10] (where DPhF = *N*,*N*′-diphenylformamidinate), have been synthesized. Complexes containing such oxo bridging groups are of interest in chemistry,[15] biochemistry,[16] magnetochemistry,[17] and catalysis.[18]

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[1] (a) Gatteschi, D.; Kahn. O.; Miller, J. S.; Palacio, F. *Molecular Magnetic Materials*; Kluwer Academic: Dordrecht, The Netherlands, 1991. (b) Kahn, O. *Molecular Magnetism*; VCH: Weinheim, Germany, 1993. (c) Miller, J. S.; Epstein, A. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *73*, 30.

[2] (a) Lim, Y. Y.; Drago, R. S. *Inorg. Chem.* **1972**, *11*, 1334. (b) Richman, R. M.; Kuechler, T. C.; Tanner, S. P.; Drago, R. S. *J. Am. Chem. Soc.* **1977**, *99*, 1055. (c) Drago. R. S.; Kuechler, T. C.; Kroeger, M. *Inorg. Chem.* **1979**, *18*, 2337. (d) Dickman, M. H.; Doedens, R. J. *Inorg. Chem.* **1981**, *20*, 2067. (e) Richardson, R. F.; Kreilick, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 8183. (f) Anderson, O. P.; Kuechler, T. C. *Inorg. Chem.* **1980**, *19*, 1417.

[3] Fujiara, H.; Kobayashi, H. *Chem. Commun.* **1999**, 2417.

[4] (a) Jaitner, P.; Huber. W.; Huttner, G.; Scheidsteger, O. *J. Organomet. Chem.* **1983**, *259*, C1. (b) Jaitner, P.; Huber, W.; Gieren, A.; Betz, H. *J. Organomet. Chem.* **1986**, *311*, 379. (c) Jaitner, P.; Huber. W. *Inorg. Chim. Acta* **1987**, *129*, L45.

[5] Preliminary results have been presented in a communication: Jaitner, P.; Rieker, C.; Wurst, K. *Chem. Commun.* **1997**, 1245.

[6] Cotton. F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999.

[7] (a) Bragg, W.; Morgan, G. T. *Proc. R. Soc. London, Ser. A* **1923**, *104*, 437. (b) Tulinsky, A.; Worthington, C. R.; Pignataro, E. *Acta Crystallogr.* **1959**, *12*, 623. (c) Tulinsky, A. *Acta Crystallogr.* **1959**, *12*, 634. (d) Tulinsky, A.; Worthington, C. R. *Acta Crystallogr.* **1959**, *12*, 626.

[8] (a) Koyama, H.; Saito, Y. *Bull. Chem. Soc. Jpn.* **1964**, *27*, 112. (b) Hiltunen, L.; Leskela, M.; Mäkelä, M.; Niinstö.; L. *Acta Chem. Scand.* **1987**, *A41*, 548.

[9] (a) Clegg, W.; Harbron, D. R.; Homan, C. D.; Hunt. P. A.; Little, I. R.; Sraughan, B. P. *Inorg. Chim. Acta* **1987**, *129*, L45.

[10] (a) Cotton, F. A.; Daniels, L. M.; Falvello, L. R.; Matonic, J. H.; Murillo, C. A.; Wang, X.; Zhou, H. *Inorg. Chim. Acta* **1991**, *186*, 51. (b) Belforte, A.; Calderazzo, F.; Englert, U.; Strähle, J. *Inorg. Chem.* **1991**, *30*, 3778. (c) Lee, C. F.; Chin, (d) Konno, T.; Okamoto, K.; Hidaka, J. *Inorg. Chem.* **1994**, *33*, 538.

[11] Cotton, F. A.; Murillo, C. A.; Pascual, I. *Inorg. Chem.* **1999**, *38*, 2746.

[12] Blake, A. B. *Chem. Commun.* **1966**, 569.

[13] Okamoto, K. I.; Konno, T.; Hidaka, J. *J. Chem. Soc. Dalton Trans.* **1994**, 533.

[14] Sturgeon, R. L.; Olmstead, M. M.; Schore, N. E. *Organometallics* **1991**, *10*, 1649.

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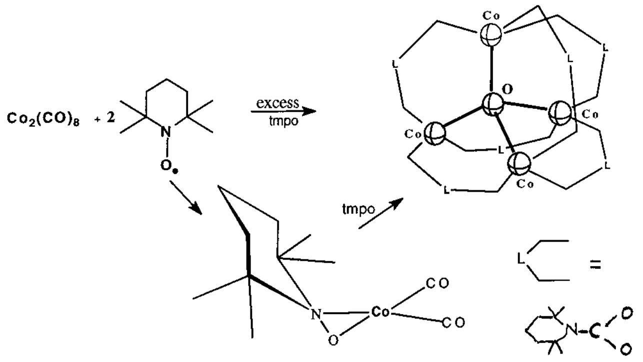
Scheme 1



Results and Discussion

Synthesis. Photolysis of $Co_2(CO)_8$ promotes the fission of the Co−Co bond to generate the radical $Co(CO)_4^\bullet$. This radical reacts with an equimolar amount of tmpo to yield $[Co(CO)_2(tmpo)]$ (**1**).[4b] Surprisingly, when a 4-fold excess of tmpo was used at room temperature in a reaction with $[Co_2(CO)_8]$, in pentane or benzene in the dark, the blue carbamato complex $[Co_4(\mu_4\text{-}O)(OOCNC_9H_{18})_6]$ (**2**) was formed in high yield (>80%). When the reaction of $Co_2(CO)_8$ with tmpo is carried out in the absence of solvent, a blue complex characterized as **2** is formed in high yield.

The mechanism of formation of **2** is not completely understood. However, it can be inferred that, to promote a simultaneous oxo transfer and CO insertion into the radical tmpo, an excess of tmpo is required. To explain this, a cascade type reaction in which complex **1** is formed as an intermediate and the tmpo radical acts as an oxidizing agent may be postulated. To test the viability of this mechanism, complex **1** was treated with an excess of tmpo. The resulting product was characterized as **2**, which supports the possibility of generating complex **2** from the monomer $[Co(CO)_2(tmpo)]$ (**1**), as shown in Scheme 1.

X-ray Structure of Complex 2. Single crystals (deep blue plates) of **2** were obtained using a crystallization box equipped with a heating block, as described by Hulliger.[19] Complex **2** crystallizes in the monoclinic space $P2_1/n$ with $Z = 8$. A view of the molecular structure is shown in Figure 1. Crystal data and data collection and refinement parameters are given in Table 1.

The molecular structure consists of an oxo-centered tetrahedon of Co^{II} ions. Each Co atom is bonded to the central oxygen atom and to bridging oxygen atoms of the carbamato ligands, giving a slightly distorted pyramidal coordination to each cobalt ion. The Co−O distances are Co(1)−O(1) = 1.932(11) Å, Co(2)−O(1) = 1.955(10) Å, Co(3)−O(1) = 1.952(9) Å, and Co(4)−O(1) = 1.934(9) Å. These distances are close to to those found for other similar complexes reported in the literature which contain the $Co_4(\mu_4\text{-}O)$ unit: $[\{Ir(aet)_3\}_4Co_4O]Br_6$,[13] $[Co_4O(O_2CCCo_3(CO)_9)_6]$,[14] and recently $[Co_4O(DPhF)_6]$,[10] with cobalt−oxygen bond lengths ranging from 1.9 to 1.96 Å as in the title compound.

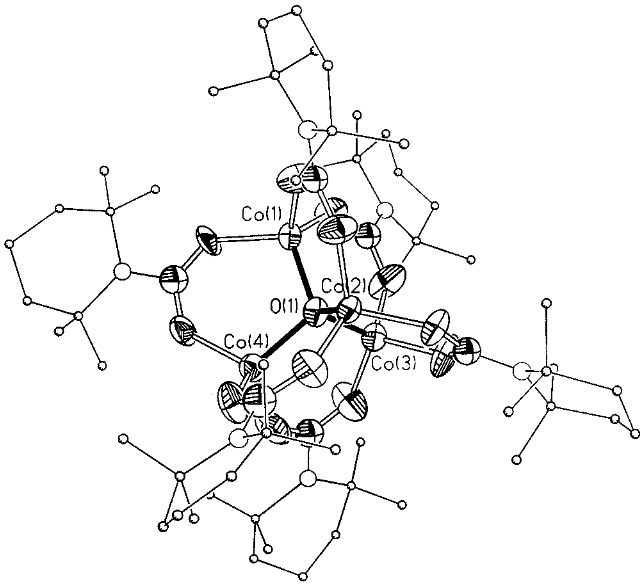


Figure 1. Molecular structure of **2**. Selected distances (Å) and angles (deg): Co(1)−O(1) = 1.932(11), Co(2)−O(1) = 1.955(10), Co(3)−O(1) = 1.952(9), Co(4)−O(1) = 1.934(9); Co(1)−O(1)−Co(4) = 111.9(5), Co(4)−O(1)−Co(3) = 107.8(4), Co(4)−O(1)−Co(2) = 108.2(5), Co(1)−O(1)−Co(3) = 108.4(5), Co(1)−O(1)−Co(2) = 110.3(4), Co(3)−O(1)−Co(2) = 110.2(5).

Table 1. Crystal Data and Sructure Refinement Details for 2

mol formula	$C_{60}H_{108}Co_4N_6O_{13}$
fw	1357.24
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
unit cell dimens	
a	20.838(5) Å
b	29.647(7) Å
c	25.407(6) Å
β	114.20(1)°
V	14 317(6) Å^3
Z	8
temp	193(2) K
radiation	Mo Kα (λ = 0.710 73 Å)
density (calcd)	1.259 g/m^3
abs coeff	0.969 mm^{-1}
F(000)	5776
color, habit	blue prism
cryst size	0.5 × 0.4 × 0.3 mm
θ range for data collection	2.06−19.0°
no. of rflns collected	11 156
no. of indep rflns	10 041
no. of rflns with $I > 2\sigma(I)$	7092
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	10 041/0/897
goodness of fit on F^2	1.055
final R indices ($I > 2\sigma(I)$)	R1 = 0.0802, wR2 = 0.2011
largest diff peak and hole	0.956 and −0.535 e Å^{-3}

NMR Experiments. The ^{13}C NMR spectrum of complex **2** consists of a pattern of sharp signals resembling those previously observed in the ^{13}C NMR spectrum of complex **1**. Indeed, all the ^{13}C NMR signals of **2** are sharp doublets, indicating a diastereotopic arrangement of the carbamato ligands in solution (see the Experimental Section).[20]

Magnetic Susceptibility Experiments. Variable-temperature magnetic susceptibility data over the range 1.8−320 K and 1 T applied magnetic field were obtained for **2**. The sample was restrained in a solid matrix of eicosane to prevent torquing, and the experimental

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(15) (a) Bottomley, F. *Polyhedron* **1992**, *11*, 1707. (b) West, B. O. *Polyhedron* **1989**, *8*, 219.

(16) Anderson, K.K.; Graslund, A. *Adv. Inorg. Chem.* **1995**, *43*, 359.

(17) Murray, K. S. *Adv. Inorg. Chem.* **1995**, *43*, 261.

(18) Ladas, S.; Imbihl, R.; Ertl, G. *Surf. Sci.* **1989**, *219*, 88; **1993**, *280*, 14.

(19) Hulliger, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 143.

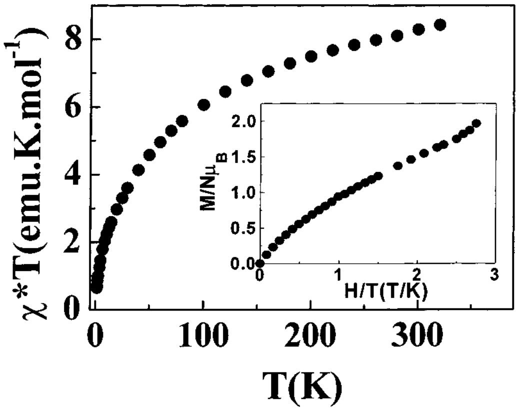

Figure 2. Plot of the solid-state magnetic moment of **2** vs temperature.

susceptibility data were corrected for the underlying diamagnetism using background measurements and Pascal constants. The plot of the effective magnetic moment vs *T* is shown in Figure 2. The effective magnetic moment decreases gradually from 8.10 emu K mol^{-1} at 320 K to 4.23 emu K mol^{-1} at 50 K; the value thereupon decreases more abruptly to 0.58 emu K mol^{-1} at 1.8 K.

The effective magnetic moment found at 320 K is consistent with the spin-only value 7.5 emu K mol^{-1} ($g = 2$) expected for four uncoupled high-spin Co(II) ions, although the value is slightly greater on account of second-order spin−orbit coupling effects. The dependence of the magnetization on the field was also studied. Variable-field magnetic data have been collected for complex **2** in the range of 0.1−50 kG at low temperatures (1.8−10 K). The $M/N\mu_B$ vs H/T plots determined at different fields cannot be superimposed, a result that is consistent with (i) spin−orbit coupling and low-symmetry crystal field effects characteristics of Co(II) ions,[22] (ii) population of thermally accessible magnetic excited states, even at low temperatures (1.8 K), and, most likely, (iii) a combination of both effects. Indeed, the dependence of $M/N\mu_B$ on the field at 1.8 K for complex **2** (see insert of Figure 2) exhibits a clear inflection and consequently does not follow the Brillouin function.

The theoretical analysis for **2** has not been carried out because of the complexity of the spin states that arise from the four cobalt ions and the combined action of spin−orbit coupling and low-symmetry crystal field effects. It is clear, however, that the decrease of the effective magnetic moment with temperature in the χT vs *T* plot is consistent with the presence of antiferromagnetic interactions between pairs of Co(II) ions and to some extent of spin−orbit coupling effects. Similar antiferromagnetic interactions between the cobalt ions were observed in the related [$Co_4(\mu_4\text{-}O)(acetate)_6$] cluster reported by Blake.[12] Indeed, the χT vs *T* plot of this cluster showed an unusually low effective magnetic moment at room temperature, attributed to the presence of strong antiferromagnetic exchange interactions between the four magnetic Co(II) ions through the central oxygen bridge.

Assuming that the magnetic exchange interactions are propagated via superexchange mechanism involving the μ_4-O moiety and to a lesser extent by the O−C−O pathway, it can be postulated that μ_4-O in **2** is favoring antiferromagnetic magnetic exchange interactions between pairs of Co(II) ions. Such antiferromagnetic interactions are presumably originated by the high Co−O−Co bond angles that range between 107.8(4) and 119.0(5)°. Such angles differ considerably from 90°, for which ferromagnetic interactions are expected.[13] Similar angular dependence of the magnetic exchange interactions between Co(II) ions has been reported in a related dinuclear complex.[21] Indeed, the temperature magnetic susceptibility data of the complex [$Co_2(DBA)_2(py)$]·4py, where DBA is 1,5-diphenyl-1,3,5-pentanetrionato and py is pyridine, indicate strong antiferromagnetic interactions between the cobalts via superexchange of the bridging oxygen atoms, where the Co−O−Co bond angle is 103°.

Experimental Section

General Remarks. All solvents were reagent grade and were distilled, unless otherwise indicated. All reagents, organic and inorganic, were of high-purity grade. Direct current (dc) magnetic susceptibility measurements were carried out on a Quantum Design MPMS SQUID susceptometer with a 55 kG magnet and operating in the range of 1.7−320 K. All measurements were collected in a field of 10 kG. Background correction data were collected from magnetic susceptibility measurements on the holder capsules. Diamagnetic corrections estimated from the Pascal contents were applied to all data for determination of the molar paramagnetic susceptibilities of the compounds.

Synthesis of [$Co(CO)_2tmpo$] (1). We have reprepared the compound **1** to provide a complete set of NMR data.[4b] The ^1H NMR of the hydroxylamido compound **1** shows diastereotopic protons of the different methyl groups located at 0.98 and 1.26 ppm.[21] In the ^{13}C NMR of **1** the three resonances of the piperidine carbon atoms and two diastereotopic methyl groups are present. The assignment of the ^{13}C signals has been verified by a DEPT experiment (see below). The resonances of the CO ligands are not visible, due to the large quadrupole of the Co atom, while the ^{17}O NMR spectrum shows two separated signals for the different CO groups. The distances from the Co atom and the next located H of a methyl group are 2.51 and 2.47 Å, evidencing the lack of agostic interactions between the Co ion and H.

Characterization data are as follows: red-brown crystals; mp 70 °C. ^1H NMR (C_6D_6): δ 1.22 (6H, s); 0.92 (6H, s); 1.35, 1.30, 1.10, 1.06 (unresolved multiplet). ^{13}C NMR (C_6D_6): δ 65.5 (s) C(1) and C(5), 37.9 (s) C(2) and C(4), 32.9 (s) (Me), 23.9 (s) (Me),16.7 (s) C(3); carbon atoms are denoted as shown in Figure 1 in the Supporting Information. DEPT experiments (135) show the methyl groups to be positive. ^{17}O NMR (in benzene with C_6D_6): 374, 368 ppm referenced to $H_2{}^{17}O$.

Synthesis of [$Co_4O(OOCNC_9H_{18})_6$] (2). A Schlenk tube charged with 342 mg (1.0 mmol) $Co_2(CO)_8$ and 1.25 g (8.0 mmol) 2,2,6,6-tetramethylpiperidin-1-oxyl in 40 mL of *n*-pentane (or benzene) was stirred for 1 h. After a few minutes a color change from brown to deep blue occurred. Crystalliza-

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(20) The pioneering work of Wieghardt, concerning the configuration isomerism of N,N′-disubstituted (hydroxylamido)molybdenum(VI) complexes, had already proved the existence of diastereotopic H atoms in such systems: Hofer, E.; Holzbach, W.; Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 282.

(21) Kuszaj, J. M.; Tomlonovic, B.; Murtha, D. P.; Linvedt, R. L.; Glick, M. D. *Inorg. Chem.* **1973**, *12*, 1297.

(22) In the case where only the ground state is populated, the zero field splitting parameter *D* and the *g* value can be determined from the $M/N\mu_B$ versus H/T plots obtained at different fields and temperatures. See: Aubin, S. M. J.; Wemple, M. W.; Adams, D. M.; Tsai, H.-L.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1996**, *118*, 7746.

tion gave **2** in 82% yield. Thin-layer chromatography confirmed the purity and presence of only one compound.

When the reaction of $Co_2(CO)_8$ with tmpo was carried out in the absence of solvent, a blue complex characterized by infrared spectroscopy as **2** was formed in high yield.

Anal. Calcd for $C_{60}H_{108}Co_4N_6O_{13}$: C, 53.09, H, 8.02. Found: C, 52.7; H, 7.7. IR (KBr, cm^{-1}): 2967, 2931, 2867, 1715, 1616, 1459, 1402, 1374, 1275, 1161, 1132, 1054, 876, 834, 791, 492. ^1H NMR (C_6D_6): δ 1.57 (s); 1.36 (s); 1.22 (s). ^{13}C NMR (C_6D_6): δ 59.7 (s), 56.1 (s), 40.6 (s), 40.3 (s), 31.9 (s), 30.6 (s), 22.3 (s), 17.4 (s), 15.9 (s).

X-ray Crystallographic Study of 2. X-ray data were collected at 193 K, on a Bruker P4 diffractometer with monochromatic Mo Kα ($\lambda = 0.710\ 73$ Å) radiation. Data were collected via ω scans and corrected for Lorentz and polarization effects but not for absorption. The structures were all refined by a full-matrix least-squares method. Atomic coordinates and other related structural data have been deposited as Supporting Information.

Crystallographic data (excluding structure factors) for the structure of **2** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-182/475. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax, int. code + 44-(1223)336-033; E-mail, deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Figures giving the structures of compounds **1** and **2** and tables giving details of the X-ray crystal data for compound **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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