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Notes

Synthesis and Structural Characterization of the Nitrido−Carbonyl Cluster Anion $[Co_{10}N_2(CO)_9(\mu\text{-}CO)_{10}]^{4-}$ Having an Unprecedented Metal Cage Built of Three Condensed Trigonal Prisms

Alessandro Fumagalli,*,[†] Secondo Martinengo,[‡] Massimo Tasselli,[‡] Gianfranco Ciani,[§] Piero Macchi,[§] and Angelo Sironi*,[§]

CNR−Centro di Studio sulla Sintesi e la Struttura dei Composti dei Metalli di Transizione nei Bassi Stati di Ossidazione, Dipartimento di Chimica Inorganica Metallorganica e Analitica, and Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università di Milano, Via G. Venezian 21, 20133 Milano, Italy

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Introduction

Interstitial main group atoms (C, N, P, etc.) play an essential role in the buildup of high-nuclearity metal carbonyl clusters because, unlike conventional ligands, they can contribute to the number of cluster valence electrons with no sterical requirements on the cluster surface.[1] In this respect, nitrido species are particularly interesting, since nitrogen atoms may donate up to five electrons, and also show a distinctive aptitude toward unusual stereochemistries and coordination numbers within the interstitial cavity; this results in singular cluster shapes. Several examples of nitrido and polynitrido clusters have been reported, mostly of rhodium, from the precursor of them all, $[Rh_6N(CO)_{15}]^-$,[2] up to the recently reported giant $[Rh_{28}N_4(CO)_{41}H_x]^{4-}$.[3] Not so many are interstitial nitrido species of cobalt; to date only four compounds, $[Co_6N(CO)_{15}]^-$,[4] $[Co_6N(CO)_{13}]^-$,[5] $[Co_7N(CO)_{15}]^{2-}$,[6] and $[Co_{14}N_3(CO)_{26}]^{3-}$,[7] have been reported.[8] To uncover similarities and peculiarities of cobalt chemistry compared to rhodium chemistry, we reinvestigated the reactivity of $[Co_6N(CO)_{15}]^-$ which afforded the presently reported dinitrido cluster $[Co_{10}N_2(CO)_{19}]^{4-}$

Table 1. Crystallographic Data for $[Co_{10}N_2(CO)_{19}][NMe_3CH_2Ph]_4\cdot 0.5MeCN\cdot 0.5Me_2CO$

chemical formula	$Co_{20}N_{13}C_{133}O_{39}H_{137}$	fw	3586.99
a	14.095(1) Å	μ	2.340 mm^{-1}
b	40.112(1) Å	ρ_{calc}	1.675 g/cm^3
c	14.297(1) Å	T	170 K
β	118.38(1)	λ	0.7107 Å
V	7111.4(2) Å^3	R_1 (F_o)	0.0321
Z	2[a]	$[F_o > 4\sigma(F_o)]$[b]	
space group	$P2_1$ (No. 4)	wR (F_o^2) $[F_o > 4\sigma(F_o)]$[c]	0.0532

[a] The asymmetric unit contains two different clathrated molecules (MeCN and Me_2CO) and this does not allow to indicate Z as 4. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = (\sum(F_o^2 - F_c^2)^2/\sum wF_o^4)^{1/2}$. [c] Weighting: $w = 1/[\sigma^2(F_o^2) + (0.0188P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

Experimental Section

General Procedures and Materials. All operations were carried out under N_2 or CO as specified, with standard Schlenk-tube apparatus. Tetrahydrofuran (THF) was distilled from Na-benzophenone and 2-propanol from Al isopropoxide. All other analytical grade solvents were degassed and stored under N_2. $K[Co_6N(CO)_{15}]$ was prepared by the published method.[4] Infrared spectra were recorded in solution with CaF_2 cells (0.1 mm; 0.075 mm for water solutions) previously purged with nitrogen, on a Perkin-Elmer 16 PC FT-IR spectrophotometer, ^{13}C NMR spectra were recorded at 50.3 MHz on a Varian instrument.

Synthesis of $[NMe_3CH_2Ph]_4[Co_{10}N_2(CO)_{19}]$. $K[Co_6N(CO)_{15}]$ (0.378 g, 0.457 mmol) was treated with an aqueous solution of NaOH (1.3 M, 15 mL) and the resulting suspension was stirred at room temperature for ca. 30 min, up to formation of a dark brown solution. After filtration of some insoluble material, the clear solution was treated dropwise, while stirring, with an aqueous solution of $[NMe_3CH_2Ph]Cl$ (0.5 g in 5 mL); this caused immediate formation of a brown precipitate, which after a few minutes of stirring, was filtered, thoroughly washed with water (4 × 5 mL), and vacuum-dried. The crude product contained some $[Co(CO)_4]^-$ which was mostly extracted with a few THF washings; the residue was dissolved in acetone (6 mL) and after addition of MeCN (3 mL), was cautiously layered with 2-propanol (25 mL). When the diffusion of the solvents was complete (about a week), the slightly brown mother liquor was syringed off and the black crystals were washed with 2-propanol and vacuum-dried. Yield: 0.212 g, 50%. The crystals suitable for the X-ray analysis contained one MeCN and one acetone molecule for every 2 mol of product. Anal. Found (calcd) for $[NMe_3CH_2Ph]_4[Co_{10}N_2(CO)_{19}]\cdot 0.5MeCN\cdot 0.5(CH_3)_2CO$: C, 44.03 (41.04); H, 4.13 (3.84); N, 5.51 (5.06). The presence of $[NMe_3CH_2Ph][Co(CO)_4]$ as an impurity may be checked by the strong IR band at 1893 cm^{-1}; in that case a recrystallization is suggested.

The Cs^+ salt is a useful starting material and may be obtained with comparable yields by addition of excess CsCl to the aqueous reaction solution, filtration, washing with 2% CsCl, and vacuum-drying. It can be converted by metathesis in several derivatives of different cations such as the $[NMe_4]^+$ salt. Anal. Found (calcd) for $[NMe_4][Co_{10}N_2(CO)_{19}]$: C, 29.0 (29.07); H, 4.36 (3.35); N, 5.61 (5.81).

X-ray Structure Determination. A crystal sample of dimensions 0.12 × 0.16 × 0.30 mm was mounted on a glass fiber in air[9] and collected at $T = 170$ K on a Siemens SMART CCD area-detector diffractometer. Crystal data are reported in Table 1. Graphite-monochromatized Mo Kα ($\lambda = 0.710\,73$ Å) radiation was used with the generator working at 50 kV and 35 mA. The cell parameters and

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[†] CNR.

[‡] CIMA, Università di Milano.

[§] CSSI, Università di Milano.

(1) As a cluster grows, the maximum allowed number of carbonyls per metal atom decreases only for sterical reasons: Chini, P. *Gazz. Chim. Ital.* **1979**, *109*, 225.

(2) Bonfichi, R.; Ciani, G.; Sironi, A.; Martinengo, S. *J. Chem. Soc., Dalton Trans.* **1983**, 253.

(3) Fumagalli, A.; Martinengo, S.; Bernasconi, G.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Am. Chem. Soc.* **1997**, *119*, 1450 and references therein.

(4) Martinengo, S.; Ciani, G.; Sironi, A.; Heaton, B. T.; Mason, J. *J. Am. Chem. Soc.* **1979**, *101*, 7095.

(5) Ciani, G.; Martinengo, S. *J. Organomet. Chem.* **1986**, *306*, C49.

(6) Ciani, G.; Masciocchi, N.; Sironi, A.; Fumagalli, A.; Martinengo, S. *Inorg. Chem.* **1992**, *31*, 331.

(7) Martinengo, S.; Ciani, G.; Sironi, A. *J. Organomet. Chem.* **1988**, *358*, C23.

(8) A mixed Co and Mo cluster with a semiexposed nitrido ligand has been reported: Gibson, C. P.; Dahl, L. F. *Organometallics* **1988**, *7*, 543.

(9) Although **1** is air-sensitive in solution and as a powder, its crystals can be mounted in air; during the data-collection, carried out at 170 K, the sample was protected by the cooling N_2 stream.

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the orientation matrix were obtained from least-squares refinement on 302 reflections measured in three different sets of 15 frames each, in the range $0 < \theta < 23°$. The intensity data were collected within the limits $8 < 2\theta < 50°$ in the full sphere (ω scan method), with the sample−detector distance fixed at 7 cm, thus avoiding the possible overlap of spots due to the great cell volume. In all, 2100 frames (20 s per frame; $\Delta\omega = 0.3°$) were collected; the first 100 frames, containing 859 reflections, were recollected to have a monitoring of crystal decay, which was not observed; an absorption correction was applied (SADABS[10]). A total of 46 254 reflections were collected (24 238 unique, $R_{\mathrm{int}} = 0.0284$; $R_\sigma = 0.0540$[11]). The structure was solved by direct methods (SIR97[12]) and refined with full-matrix-block least squares (SHELX93[13]) on the basis of 21 254 independent reflections with $I > 2\sigma(I)$; anisotropic temperature factors were assigned to all non-hydrogen atoms. Hydrogens were riding on their carbon atoms.

$[Co_{10}N_2(CO)_{19}]^{4-}$ is, at least in the solid state, chiral. However, its $[NMe_3CH_2Ph]^+$ salt crystallizes as a racemate in the noncentric space group $P2_1$ with two independent (enantiomeric) anions in the asymmetric unit (which contains also eight cations and two *different* clathrated solvent molecules). We have carefully checked for the presence of some "missing" symmetry element eventually affording a centrosymmetric group, but we did not find it: the two enantiomeric molecules are not correlated by any *extra crystallographic* symmetry operation; moreover, the intensities statistic suggests the lack of a center of symmetry.

The final conventional agreement indexes R_1 and wR_2 for the "best" structural enantiomer were 0.0321 and 0.0532 ($F_o > 4\sigma(F_o)$) and 0.0415 and 0.0558 (all data), respectively, while the "worst" structural enantiomer gave 0.0418 and 0.0776 ($F_o > 4\sigma(F_o)$) and 0.0513 and 0.0797 for all data ($R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2 = (\Sigma(F_o^2 - F_c^2)^2/\Sigma wF_o^4)^{1/2}$).

Results and Discussion

Treatment of $K[Co_6N(CO)_{15}]$ with aqueous NaOH (1.3 M) yields within minutes at room temperature a solution from which the anion $[Co_{10}N_2(CO)_{19}]^{4-}$ (**1**) can be isolated as the Cs^+, $[NMe_4]^+$, or $[NMe_3CH_2Ph]^+$ salts. The side formation of $[Co(CO)_4]^-$ is consistent with the formal stoichiometry (1):

$$2[Co_6N(CO)_{15}]^- + 8OH^- \rightarrow [Co_{10}N_2(CO)_{19}]^{4-} + 2[Co(CO)_4]^- + 2[CO_3]^{2-} + 4H_2O + CO \quad (1)$$

In the same conditions $[Rh_6N(CO)_{15}]^-$ yields $[Rh_6N(CO)_{14}H]^{2-}$,[14] which only at considerably higher concentrations of base (>10 M) gives what has been identified as $[Rh_6N(CO)_{14}]^{3-}$.[15]

All the salts of **1** show the same IR spectrum in MeCN: 1987 w, 1934 s, 1890 mw, 1798 m, 1775 ms, 1730 w ± 2 cm^{-1}.

NMR spectra were done on both the $[NMe_4]^+$ and $[NMe_3CH_2Ph]^+$ salts in d_3-MeCN at 295 and 238 K, close to the freezing point of the solution. ^1H spectra (200 and 300 MHz) did not show any resonance due to the presence of hydride(s) in the range $\delta = +38$ to -50 ppm. Natural abundance ^{13}C spectra showed at room-temperature two broad peaks at 244.4 and 236.2 ppm whose relative intensities fit for 2 and 17 carbonyls, respectively; this is consistent with a fluxional behavior that does not involve the whole molecule. When the temperature is lowered, the peak at 236.2 ppm coalesces without evidence of a static structure.

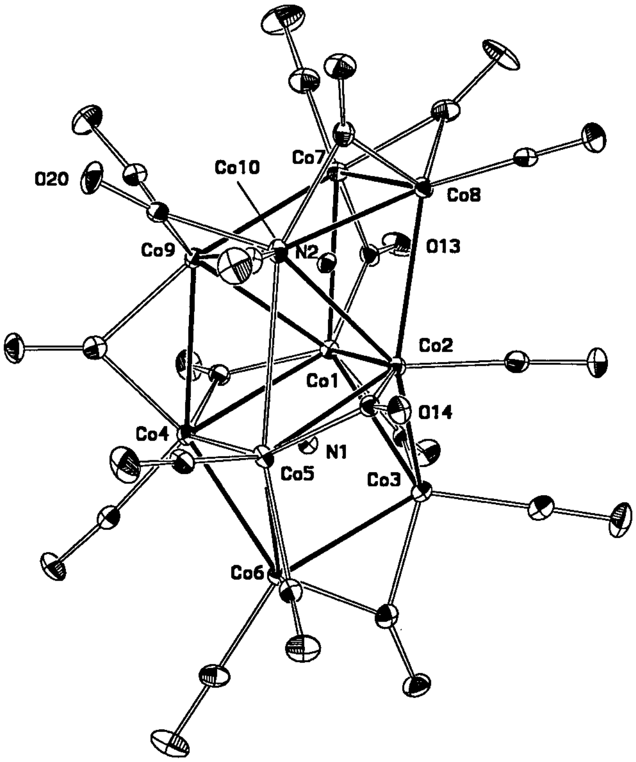

Figure 1. View of the anion $[Co_{10}N_2(CO)_{19}]^{4-}$ (ellipsoids are drawn at 50% probability level). The two long Co−Co bond distances are represented as white sticks; all carbonyl labels but the three quoted in the text (indicated by their oxygen atom only) are omitted. Co−Co bond distances in Å (averaged over the two enantiomers; σ_{n-1} in parentheses) are as follows: *1−2*, 2.628(4); *1−3*, 2.553(7); *1−4*, 2.518(6); *1−7*, 2.572(8); *1−9*, 2.666(8); *2−3*, 2.547(30); *2−5*, 2.469(3); *2−8*, 2.610(7); *2−10*, 2.603(13); *3−6*, 2.511(3); *4−5*, 2.792(44); *4−6*, 2.540(13); *4−9*, 2.580(40); *5−6*, 2.531(16); *5−10*, 2.922(72); *7−8*, 2.490(5); *7−9*, 2.593(30); *8−10*, 2.530(4); *1−3*, 2.553(7); *9−10*, 2.524(2). Average $Co-C_{\mathrm{terminal}}$ distance: 1.754(9) Å. Average $Co-C_{\mathrm{bridging}}$ distance: 1.924(24) Å. Individual ESDs are less than 0.001 Å.

1 is very air-sensitive both in solid (as a powder) and in solution (MeCN and acetone) and also very reactive toward CO, which induces a multistep reaction. A solution of **1** in MeCN was treated at room temperature with several small amounts of CO (injected with a gas-tight syringe trough a rubber septum). IR spectra, taken after each addition (allowing a few minutes of stirring for equilibration), showed that ca. 2 mol of CO per mole of **1** is required for complete reaction, yielding $[Co(CO)_4]^-$ and an unknown intermediate anion (IR absorptions at 1974 s, 1954 ms, 1803 m, 1765 mw cm^{-1}). Further gradual addition of excess CO (up to 10 mol of CO per mole of **1**) eventually gave a mixture of $[Co_6N(CO)_{15}]^-$ and $[Co(CO)_4]^-$.

The structure of the tetraanion $[Co_{10}N_2(CO)_{19}]^{4-}$ is illustrated in Figure 1. The unprecedented metal cage is built from two trigonal prismatic units (1 and 2, each containing an interstitial nitrogen atom, N1 and N2, respectively) sharing the common edge Co1−Co2. The novelty of the cluster shape arises from this edge being *intrabasal* for unit 1 and *interbasal* for unit 2 (see Figure 1). The presence of two interprismatic bonds (Co4−Co9 and Co5−Co10) results in a third (empty) prismatic unit. There are nine terminal carbonyl ligands: one for each cobalt atom except Co1. There are ten double bridging carbonyls: five on unit 1, four on unit 2, and one on the interprismatic Co4−Co9 connection. Each cobalt atom bears two bridging COs, but Co1 and Co2 bear three and one, respectively.

The metal cage could have an idealized C_s symmetry;

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[10] Sheldrick, G. M. *SADABS*; University of Göttingen: Germany, to be published.

[11] $R_{\mathrm{int}} = \Sigma|F_o^2 - F_{\mathrm{mean}}^2|/\Sigma F_o^2$; $R_\sigma = \Sigma\sigma(F_o^2)/\Sigma F_o^2$.

[12] Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *24*, 435.

[13] Sheldrick, G. M. 1993 *SHELX93*: *Program for the Refinement of Crystal Structure*; University of Göttingen: Germany, 1993.

[14] Ciani, G.; Proserpio, D. M.; Sironi, A.; Martinengo, S.; Fumagalli, A. *J. Chem. Soc., Dalton Trans.* **1994**, 471.

[15] S. Martinengo and A. Fumagalli, unpublished results.

however, the actual carbonyl disposition, of C_1 symmetry, promotes significant distortions of otherwise equivalent Co−Co interactions, thus reducing also the cage symmetry to C_1.

$[Co_{10}N_2(CO)_{19}]^{4-}$, with 142 cluster valence electrons, conforms to the EAN rule if the two moderately long Co4−Co5 and Co5−Co10 interactions (average 2.79 and 2.92 Å, respectively) are also considered as bonds. As for the local electron count, Co1 and Co2 can be considered to be more electron rich than Co4, Co5, Co9, and Co10 which on the other hand, are more electron rich than Co3, Co6, Co7, and Co8. Carbonyls bridging "electron rich" and "electron poor" metal atoms are expected to be distorted toward the poor ones,[16] and this holds for all but CO(13), CO(14), and CO(20) which are symmetric or have the opposite behavior. Indeed, the localization of some anionic charge on Co5 and Co10 would explain both the "anomalous" behavior of these same CO ligands and the long Co4−Co5 and Co5−Co10 distances.

Finally, we would like to comment on the overall size and distortion of the three prismatic cavities which, given the nonuniform distribution of the bridging COs, are all rather distorted. However, the cavity containing N1 is clearly more regular than that containing N2 because in the former all the interbasal edges are bridged. Moreover, the empty cavity which, lacking the interstitial nitride, could be the smallest, is clearly the biggest, at least judging from the average Co−Co bond distance (2.565 and 2.579 for units 1 and 2 respectively, 2.633 Å for the empty cavity) or from the fact that the interprismatic bonds are the longest metal−metal interactions within their classes (Co4−Co9 among the bridged and Co5−Co10 among the unbridged).

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles (15 pages). Ordering information is given to any current masthead page.

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[16] Sironi, A. *Inorg. Chem.* **1995**, *34*, 1342.