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# Notes

## The Nonexistent Crystals of Macrocyclic Nickel(III). Structure of the Cobalt(III) Complex of 1,4,7-Triazacyclononane-*N*,*N*′,*N*″-triacetate

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### Introduction

The existence of a nickel(III) complex of 1,4,7-triazacyclononane-N,N′,N″-triacetate (TCNTA), inferred from the crystallographic study[1] of a crystal that appeared after many months in a nitric acid solution of $Ni(NO_3)_2$ and TCNTA, has never been confirmed by electrochemical means or by any other independent study. It came to our attention that several such (unpublished) attempts have in fact failed, and this prompted a reinvestigation, using the one crystal preserved in our laboratory.

### Experimental Section

A nondestructive analysis by energy-dispersive spectroscopy, using a JSM-5400 scanning electron microscope at the Research Laboratory of the Anglo American Platinum Corp., failed to detect any nickel but established the presence of cobalt instead.

Two independent refinements of the structure, based on the structure factors reported previously,[1] were carried out, using nickel and cobalt scattering factors, respectively. Because of the small one-electron difference between the two metals, the observed differences were small but were consistently in favor of cobalt as the central metal. All hydrogens could be placed by difference-Fourier synthesis, but since a few would not refine properly by least squares, they were all linked at a common refinable distance to, and with the displacement parameters of, their respective carbon atoms.

Crystallographic data are listed in Table 1 and refined atomic parameters in Table 2, according to the numbering scheme shown in Figure 1. Figure 2 is a stereoscopic drawing of one of the three equivalent molecules in the asymmetric unit.

**Table 1.** Crystal Data for $Co(TCNTA)_3$

| | | | |
|---|---|---|---|
| chem formula | $C_{12}H_{18}O_6N_3Co$ | $\lambda$, Å | 0.710 69 |
| fw | 359.21 | $T$, °C | 25 |
| space group | P3c1 | $\rho_{calcd}$, g cm$^{-3}$ | 1.76 |
| $a$, Å | 13.670(7) | $\rho_{obsd}$, g cm$^{-3}$ | 1.77 |
| $c$, Å | 12.586(6) | $\mu$(Mo Kα) cm$^{-1}$ | 12.19 |
| $V$, Å$^3$ | 2036.8(5) | $R^a$ ($F_o$) | 0.051 |
| Z | 6 | $R_w{}^b$ ($F_o$) | 0.051 |

$^a$ $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b$ $R_w = \Sigma w^{1/2}||F_o| - |F_c||/\Sigma w^{1/2}|F_o|$.

**Table 2.** Atomic Coordinates (and Esd's) for $Co(TCNTA)_3$

| atom | x/a | y/b | z/c | atom | x/a | y/b | z/c |
|---|---|---|---|---|---|---|---|
| Co1 | 0.0000 | 0.0000 | 0.5000 | H222 | 0.1436 | 0.7345 | 0.3456 |
| | 0.0000 | 0.0000 | 0.0000 | | 0.0033 | 0.0069 | 0.0079 |
| O11 | 0.0949 | 0.1285 | 0.4137 | C32 | 0.1601 | 0.6207 | 0.4836 |
| | 0.0006 | 0.0006 | 0.0005 | | 0.0009 | 0.0009 | 0.0009 |
| O21 | 0.2748 | 0.2354 | 0.3687 | H312 | 0.1326 | 0.6543 | 0.5340 |
| | 0.0007 | 0.0007 | 0.0006 | | 0.0077 | 0.0077 | 0.0061 |
| N1 | 0.1315 | 0.0501 | 0.5892 | H322 | 0.0983 | 0.5878 | 0.4339 |
| | 0.0008 | 0.0008 | 0.0007 | | 0.0057 | 0.0073 | 0.0060 |
| C11 | 0.2013 | 0.1632 | 0.4275 | C42 | 0.2012 | 0.5402 | 0.5188 |
| | 0.0008 | 0.0009 | 0.0008 | | 0.0009 | 0.0009 | 0.0008 |
| C21 | 0.2307 | 0.1098 | 0.5160 | H412 | 0.2464 | 0.5867 | 0.5768 |
| | 0.0009 | 0.0010 | 0.0008 | | 0.0071 | 0.0067 | 0.0052 |
| H211 | 0.2952 | 0.1650 | 0.5553 | H422 | 0.1269 | 0.4761 | 0.5292 |
| | 0.0052 | 0.0065 | 0.0066 | | 0.0039 | 0.0053 | 0.0077 |
| H221 | 0.2441 | 0.0533 | 0.4846 | Co3 | 0.6667 | 0.3333 | 0.3368 |
| | 0.0087 | 0.0063 | 0.0071 | | 0.0000 | 0.0000 | 0.0002 |
| C31 | 0.1282 | 0.1263 | 0.6752 | O13 | 0.7635 | 0.3021 | 0.4224 |
| | 0.0009 | 0.0010 | 0.0009 | | 0.0006 | 0.0005 | 0.0006 |
| H311 | 0.0930 | 0.0805 | 0.7369 | O23 | 0.9456 | 0.3752 | 0.4601 |
| | 0.0079 | 0.0070 | 0.0049 | | 0.0007 | 0.0007 | 0.0007 |
| H321 | 0.2077 | 0.1777 | 0.6856 | N3 | 0.7962 | 0.4172 | 0.2479 |
| | 0.0030 | 0.0070 | 0.0080 | | 0.0007 | 0.0007 | 0.0006 |
| C41 | 0.0571 | 0.1757 | 0.6403 | C13 | 0.8681 | 0.3714 | 0.4084 |
| | 0.0009 | 0.0010 | 0.0009 | | 0.0009 | 0.0008 | 0.0008 |
| H411 | 0.0365 | 0.2141 | 0.6923 | C23 | 0.8931 | 0.4603 | 0.3205 |
| | 0.0081 | 0.0077 | 0.0063 | | 0.0009 | 0.0009 | 0.0008 |
| H421 | 0.0982 | 0.2344 | 0.5889 | H213 | 0.9649 | 0.4968 | 0.2846 |
| | 0.0078 | 0.0062 | 0.0063 | | 0.0041 | 0.0080 | 0.0065 |
| Co2 | 0.3333 | 0.6667 | 0.3456 | H223 | 0.9006 | 0.5234 | 0.3611 |
| | 0.0000 | 0.0000 | 0.0002 | | 0.0085 | 0.0058 | 0.0067 |
| O12 | 0.3738 | 0.7973 | 0.2596 | C33 | 0.7826 | 0.5099 | 0.1988 |
| | 0.0006 | 0.0006 | 0.0005 | | 0.0009 | 0.0009 | 0.0009 |
| O22 | 0.3070 | 0.9112 | 0.2163 | H313 | 0.7928 | 0.5570 | 0.2596 |
| | 0.0006 | 0.0006 | 0.0006 | | 0.0088 | 0.0069 | 0.0049 |
| N2 | 0.2574 | 0.7231 | 0.4356 | H323 | 0.8486 | 0.5357 | 0.1332 |
| | 0.0007 | 0.0007 | 0.0006 | | 0.0086 | 0.0088 | 0.0079 |
| C12 | 0.3064 | 0.8374 | 0.2717 | C43 | 0.6608 | 0.4591 | 0.1642 |
| | 0.0008 | 0.0009 | 0.0008 | | 0.0010 | 0.0009 | 0.0010 |
| C22 | 0.2218 | 0.7855 | 0.3620 | H413 | 0.6313 | 0.5098 | 0.1707 |
| | 0.0010 | 0.0010 | 0.0008 | | 0.0079 | 0.0067 | 0.0085 |
| H212 | 0.2073 | 0.8327 | 0.4085 | H423 | 0.6652 | 0.4212 | 0.1015 |
| | 0.0082 | 0.0071 | 0.0064 | | 0.0095 | 0.0079 | 0.0051 |

### Results and Discussion

There are three crystallographically independent molecules in the unit cell, with the central atom on a 3-fold axis. As a consequence, there are three independent measurements of each internal parameter. Comparison of these is one criterion that was used to assess the internal consistency of the two refinements. Using nickel scattering factors, the following values were determined: $d$(M−O) = 1.91, 1.92, 1.92 Å; $d$(M−N) = 1.93, 1.94, 1.91 Å. This reversal does not occur with cobalt scattering factors, for which $d$(M−O) = 1.91, 1.92, 1.91 Å and $d$(M−N) = 1.93, 1.94, 1.92 Å. The average C−H distance of 0.96 Å in the cobalt refinement is also considered to be more realistic than the 0.93 Å value for nickel. The most extreme deviations from the average C−C, C−O, and C−N bond lengths all occurred in the nickel refinement, and the conventional *R* factors of 0.051 and 0.053, although comparable, also favored the cobalt scattering factors.

The SHELX[2] program was used for the refinements as before.[1] Residual electron densities were alike for the two refinements and probably reflect errors of measurement only.

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(1) Van der Merwe, M. J.; Boeyens, J. C. A.; Hancock, R. D. *Inorg. Chem.* **1983**, *22,* 3489.

(2) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Oxford University Press: Oxford, U.K., 1985.

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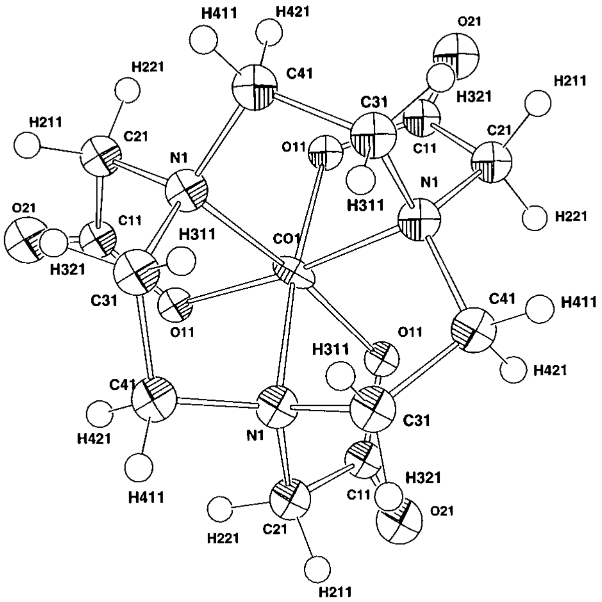

**Figure 1.** Atomic-numbering scheme for each of the three independent parts of the asymmetric unit.

It is fair to conclude that the previous report was in error and that a crystal of a cobalt rather than a nickel macrocyclic complex was isolated from the crystallization vessel.

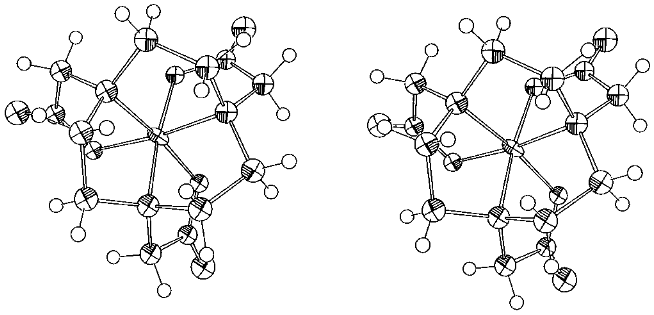

**Figure 2.** Stereoscopic view of one of the three equivalent molecules in the structure.

A detailed reconstruction of events is no longer feasible, but it seems obvious that a crystal must have grown from cobalt impurities in the nickel salt, over a period of months. It is interesting to note that contemporaneous efforts to crystallize the cobalt TCNTA complex from more concentrated solutions were unsuccessful.

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**Supporting Information Available:** Listings of atomic coordinates and displacement factors, bond distances and angles, dihedral angles, and X-ray experimental details (12 pages). Ordering information is given on any current masthead page.

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