

## Communications

**Optimum Ligand Hole Sizes for Stabilizing Nickel(III).  
Structure of the Nickel(III) Complex of  
1,4,7-Triazacyclononane-*N,N',N''*-triacetate**

Sir:

The chemistry of Ni(III) has recently received much attention.<sup>1</sup> In their study of the electrochemical oxidation of complexes of Ni(II) with N-donor macrocycles such as cyclam, Busch et al.<sup>2</sup> noted that the ease of oxidation to Ni(III) decreased as the size of the hole in the center of the macrocycle increased successively in the ligands 15-aneN<sub>4</sub> and 16-aneN<sub>4</sub>.<sup>3</sup> This was explained in terms of the idea that the Ni(II) ion should be larger than Ni(III) so that smaller cavities in the center of the macrocycle should favor the Ni(III) ion. By extrapolation, one would have expected the macrocycle 13-aneN<sub>4</sub> to favor Ni(III) over Ni(II) even more than does cyclam. However, this is not the case,<sup>2</sup> which presumably reflects the fact that the Ni(II) is able to relieve the steric compression that would be brought about by the small cavity in its 13-aneN<sub>4</sub> complex by spin-pairing and folding of the macrocycle to give octahedral forms with the two coordinated water molecules cis to each other.

We have been investigating the ligand 1,4,7-triazacyclononane-*N,N',N''*-triacetate (TACNTA), first reported by Takahashi and Takamoto,<sup>4</sup> since being hexadentate, it is able<sup>5</sup> to coordinate to metal ions octahedrally. The arrangement of the donor atoms is such that, as long as they remain coordinated, there is no way in which the metal ion can escape being compressed by folding of the ligand, as is the case with the N-donor macrocycles. Our original intention was to investigate the superior size selectivity expected for TACNTA. This expectation was borne out in that log *K*<sub>1</sub>, the formation constant of the mono complex with the small metal ion Mg(II), is over 1 order of magnitude larger than for the large metal ion Ca(II), whereas, with all other polyamino carboxylate ligands such as EDTA, the Ca(II) complexes are more stable than those with Mg(II).

The binding of TACNTA to Ni(II) is so strong that the complex H<sub>3</sub>O[Ni(TACNTA)] can be crystallized from dilute nitric acid. A crystallographic study reveals that all of the carboxylates of the TACNTA are coordinated to the Ni(II), with the hydronium ion quite separate from the complex anion. If such nitric acid solutions are allowed to stand, they slowly

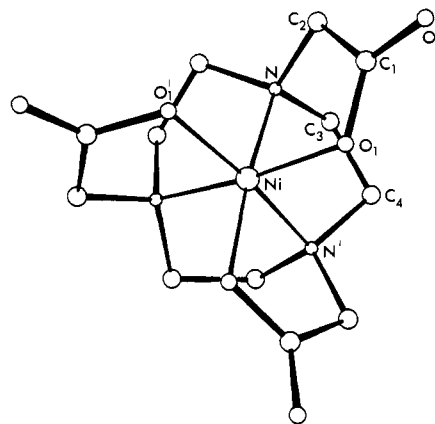


Figure 1. ORTEP<sup>10</sup> drawing of [Ni(TACNTA)], viewed down the threefold axis and showing the numbering scheme.

turn from blue to purple and finally pink and deposit pink crystals of the Ni(III) complex.

The ligand was synthesized as described,<sup>4</sup> except that it was purified by recrystallization as the monopotassium salt. The pink crystals of [Ni(TACNTA)] were obtained as described above. Preliminary X-ray analysis by photographic methods indicated the space group *P3c1*, with pseudorhombohedral conditions for the *hki0* zone, and pseudomorphism with the [Fe(TACNTA)] complex,<sup>5</sup> space group *R3c*. Accurate cell constants were measured by least-squares refinement based on the positions of 25 well-resolved reflections, measured during data collection on a Philips PW 1100 diffractometer, using Mo K $\alpha$  radiation at room temperature, *a* = 13.670 (7) and *c* = 12.586 (6) Å. The structure was solved by standard heavy-atom techniques using 986 measured intensities ( $F_{\sigma} > \sigma(F)$ ), measured in the range  $3 \leq \theta \leq 24^{\circ}$ . Data reduction consisted of background and Lorentz polarization correction only,  $\mu = 13.91$ . The structure was refined by unit-weight least-squares methods using the program SHELX<sup>6</sup> for all computations. At the termination of refinement all parameter shifts were  $< 0.5\sigma$ , *R* was 0.053, and the residual electron density nowhere exceeded  $0.5 \text{ e} \cdot \text{Å}^{-3}$ , except for a single peak of  $1.6 \text{ e} \cdot \text{Å}^{-3}$  close to one of the Ni atoms. Anisotropic thermal parameters,  $U_{ij}$ , were refined only for the three heavy atoms as coefficients in the expansion  $T = \exp[-2\pi^2 \times \sum_i \sum_j h_i h_j a_i^* a_j^* u_{ij}]$ .

A view of [Ni(TACNTA)] down the threefold axis is seen in Figure 1, and important bond lengths and angles are shown in Table I. In Table II are shown some M–N and M–O bond

- (1) Haines, R. I.; McAuley, A. *Coord. Chem. Rev.* **1981**, *39*, 77.
- (2) Busch, D. H. *Acc. Chem. Res.* **1978**, *11*, 392.
- (3) Ligand abbreviations: cyclam = 1,4,8,11-tetraazacyclotetradecane; 15-aneN<sub>4</sub> = 1,4,8,12-tetraazacyclopentadecane; 16-aneN<sub>4</sub> = 1,5,9,13-tetraazacyclohexadecane; 9-aneN<sub>3</sub> = 1,4,7-triazacyclononane; 13-aneN<sub>4</sub> = 1,4,7,10-tetraazacyclotridecane.
- (4) Takahashi, M.; Takamoto, S. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3413.
- (5) Wiegardt, K.; Bossek, U.; Chaudhuri, P.; Herrmann, W.; Menke, B. C.; Weiss, J. *Inorg. Chem.* **1982**, *21*, 4308.

- (6) Sheldrick, G. M. "SHELX Program System"; University of Cambridge: Cambridge, England, 1976.

Table I. Important Bond Lengths and Angles in [Ni(TACNTA)]<sup>a</sup>

	molecule 1	molecule 2	molecule 3
Bond Lengths			
Ni-O <sub>1</sub>	1.911 (7)	1.915 (7)	1.911 (7)
Ni-N	1.93 (1)	1.936 (8)	1.909 (8)
C <sub>1</sub> -O <sub>1</sub>	1.29 (1)	1.30 (1)	1.29 (1)
C <sub>1</sub> -O <sub>2</sub>	1.23 (1)	1.22 (1)	1.22 (1)
C <sub>1</sub> -C <sub>2</sub>	1.50 (2)	1.52 (2)	1.55 (2)
C <sub>2</sub> -N	1.50 (1)	1.49 (1)	1.47 (1)
C <sub>3</sub> -N	1.52 (2)	1.50 (1)	1.50 (1)
C <sub>3</sub> -C <sub>4</sub>	1.50 (2)	1.53 (2)	1.52 (2)
C <sub>4</sub> -N	1.53 (2)	1.49 (2)	1.50 (2)
Angles			
N-Ni-O <sub>1</sub>	85.5 (4)	85.3 (3)	85.7 (3)
C <sub>1</sub> -O <sub>1</sub> -Ni	112.8 (6)	113.5 (7)	113.7 (6)
O <sub>1</sub> -Ni-O <sub>1</sub> '	91.2 (3)	91.6 (3)	91.2 (3)
C <sub>2</sub> -N-Ni	105.4 (6)	104.7 (6)	105.0 (6)
C <sub>3</sub> -N-Ni	108.5 (7)	105.3 (7)	106.1 (6)
C <sub>3</sub> -N-C <sub>2</sub>	113.5 (9)	112.9 (9)	112.3 (8)
N-Ni-N'	89.4 (4)	89.2 (4)	89.4 (4)
O <sub>1</sub> -C <sub>1</sub> -O <sub>2</sub>	122.2 (10)	124.9 (11)	126.0 (10)
C <sub>2</sub> -C <sub>1</sub> -O <sub>1</sub>	116.3 (9)	115.0 (10)	114.1 (9)
C <sub>2</sub> -C <sub>1</sub> -O <sub>2</sub>	121.4 (9)	120.1 (10)	119.8 (10)

<sup>a</sup> Units are Å for bond lengths and deg for bond angles. For numbering scheme of atoms, see Figure 1. Numbers in parentheses are the standard deviations in the reported bond lengths and angles.

Table II. Metal to Ligand Bond Lengths and Twist Angles in TACNTA Complexes<sup>a</sup>

metal ion	M-N <sup>b</sup>	M-O <sup>b</sup>	twist angle <sup>c</sup>	ref
Ni(III)	1.93	1.91	6.9	this work
Ni(II)	2.04	2.08	12.0	<i>d</i>
Cr(III)	2.06	1.96	11.0	5
Cu(II) <sup>e</sup>	2.12	2.07	33.4	5
Fe(II) <sup>e</sup>	2.18	1.96	35.0	5 <sup>d</sup>

<sup>a</sup> For definition of the twist angle, see text. <sup>b</sup> Units are Å. <sup>c</sup> Units are deg. <sup>d</sup> Unpublished work of the present authors. <sup>e</sup> Type II structure, as discussed in text.

lengths in TACNTA complexes plus the twist angle ( $\phi$ ) around the C<sub>3</sub> axis, which is the amount by which the upper three oxygen atoms are rotated in projection relative to the lower three nitrogen atoms, from the position expected for a regular octahedron. It is seen that the structure of the Fe(III) complex is more nearly trigonal prismatic than octahedral,<sup>5</sup> since  $\phi$  would be 60° for trigonal-prismatic and 0° for octahedral coordination.

The base fragment 9-aneN<sub>3</sub> is chiral once coordinated to a metal ion, and so two possible conformers are obtainable, depending on whether the acetates attach themselves in a clockwise or anticlockwise fashion for one given arrangement of the base fragment. The structure shown for Ni(III) in the figure we designate as type I, and it is the structure found for Cr(III)<sup>5</sup> and Ni(II). We can visualize the type II structure from the figure if we detach all of the acetates, which are arranged in the figure in a clockwise fashion, and reconnect them in an anticlockwise fashion, with the conformation of the 9-aneN<sub>3</sub> base fragment remaining the same. The C<sub>2</sub> to O<sub>1</sub>' distance is considerably greater than C<sub>2</sub> to O<sub>1</sub>, and so reconnection of the acetates to give the type II structure leads to the pulling of O<sub>1</sub>' toward N and the trigonal distortion of the Fe(III) complex with  $\phi = 35^\circ$ . We have carried out an empirical force field (EFF) analysis of both the type I and II structures of the TACNTA complexes, using the EFF program described previously<sup>7</sup> and parameters for acetate groups re-

ported by Snow.<sup>8</sup> The calculations carried out with parameters appropriate for Ni(II) showed the type I structure to be about 4 kcal·mol<sup>-1</sup> more stable than the type II. The type II structure found for Fe(III)<sup>5</sup> only becomes more stable than the type I when the N-M-N, O-M-N, and O-M-O angle-bending force constants are lowered to 10% of their value for Ni(II), when type II structure is dictated by the ligand.

On completing the Ni(II) structure, the short Ni-N bond lengths of 2.04 Å, compared with the strain-free length<sup>7</sup> of 2.10 Å, suggested that oxidation to Ni(III) was being driven by release of steric strain. However, our EFF analysis shows that the best fit size for metal ions in TACNTA complexes with both type I and II structures occurs with mean metal to ligand bond lengths of 2.0 Å, and so the Ni(III) structure, with Ni-N and Ni-O bond lengths here of 1.93 and 1.91 Å, is a bit small for the TACNTA system. It would still seem, however, that a large part of the stability of [Ni(TACNTA)] derives from the fact that this is still a better fit than is found in macrocycles such as cyclam, which require metal ions with M-N bond lengths of about 2.06 Å.<sup>2,9</sup> We are at present using the EFF program to determine the metal ion size preferences of other ligands that might conceivably stabilize Ni(III), with the hope of finding some with size preferences close to the 1.90-Å metal-ligand bond lengths in which the Ni(II) cannot escape compression by spin-pairing or ligand folding and so that the Ni(III) can be stabilized as much as possible.

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**Registry No.** Ni(TACNTA), 87306-48-7; H<sub>3</sub>O[Ni(TACNTA)], 87306-49-8.

**Supplementary Material Available:** Listings of atomic coordinates, temperature factors, and observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

(8) Buckingham, D. A.; Maxwell, I. E.; Sargeson, A. M.; Snow, M. R. *J. Am. Chem. Soc.* **1970**, *92*, 3617.

(9) Hancock, R. D.; McDougall, G. J. *J. Am. Chem. Soc.* **1980**, *102*, 6551.

(10) Johnson, C. K. "ORTEP", Report No. ORNL-3794, Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

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### Electrochemical and Spectroelectrochemical Studies of Bis(peroxo)molybdenum(VI) Tetra-*m*-tolylporphyrin

Sir:

The detailed nature of the bonding of molecular oxygen to transition-metal complexes has been a subject of increasing interest because it represents a basic step in understanding the function of oxygen-carrying and -activating metalloproteins in biological systems.<sup>1-3</sup> The synthesis<sup>4</sup> and photolysis<sup>5</sup> of bis(peroxo)molybdenum(VI) tetra-*p*-tolylporphyrin, (O<sub>2</sub>)<sub>2</sub>Mo(TpTP), has recently been reported. UV irradiation

(7) McDougall, G. J.; Hancock, R. D.; Boeyens, J. C. A. *J. Chem. Soc., Dalton Trans.* **1978**, 1438.

(1) Basolo, F.; Hoffman, B. M.; Ibers, J. A. *Acc. Chem. Res.* **1975**, *8*, 384.

(2) Fuhrhop, J.-H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 648.

(3) Swedo, K. B.; Enemark, J. H. *J. Chem. Educ.* **1979**, *56*, 70.

(4) Chevrier, B.; Diebold, T.; Weiss, R. *Inorg. Chim. Acta* **1976**, *19*, L57.

(5) Ledon, H. J.; Bonnet, M. C.; Lallemand, J. Y. *J. Chem. Soc., Chem. Commun.* **1979**, 704.