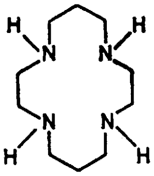
Characterization of 2,2′-Bi-(1,4,8,11-tetra-azacyclotetradecane): *X*-Ray Structure and Properties of the Dinuclear Complex $[Ni_2(C_{20}H_{46}N_8)][ClO_4]_4$

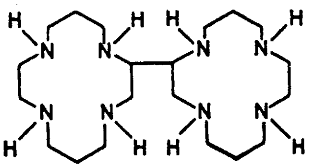
By E. KENT BAREFIELD,* DUNCAN CHUENG, and DONALD G. VAN DERVEER
(*School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia* 30332)
and FRANK WAGNER
(*Strem Chemicals, Inc., Newburyport, Massachusetts* 01950)

Summary 2,2′-Bi-(1,4,8,11-tetra-azacyclotetradecane) has been isolated as a minor product from the nickel(II)-assisted synthesis of 1,4,8,11-tetra-azacyclotetradecane (cyclam) and its structure confirmed by *X*-ray structural analysis of the dinuclear complex $[Ni_2(C_{20}H_{46}N_8)][ClO_4]_4$.

Nickel(II)-assisted cyclization reactions of linear tetra-amines with glyoxal coupled with reduction of the resulting α-di-imine (using $NaBH_4$ or H_2/Raney nickel) and decomposition with cyanide have been used for the synthesis of a variety of macrocyclic tetra-amine ligands.[1-3] The method is especially useful for the synthesis of the widely utilized ligand (**1**) (1,4,8,11-tetra-azacyclotetradecane, commonly referred to as cyclam[4]), which is obtained in yields of 60—80%.[1] A minor product has now been isolated from large-scale preparations of cyclam and identified as the dimer, 2,2′-bi-(1,4,8,11-tetra-azacyclotetradecane) (**2**). This ligand can be used to prepare a variety of dinuclear metal complexes.



(1)



(2)

In a typical preparation of the octa-amine, a mixture of $NiCl_2{\cdot}6H_2O$ (3·4 mol), 1,5,8,12-tetra-azadodecane, (3·4 mol), 40% aqueous glyoxal (500 g), and water (10 l) was left for 12 h and was then hydrogenated (1000 lb in^{-2} H_2) for 48 h at 40—50 °C with Grace Grade 28 Raney nickel catalyst. During decomposition of the macrocyclic nickel complexes with NaCN (according to the procedure given in ref. 2), a white solid precipitated† which was filtered off and air-dried (typically 10—20 g or 1·5—3%). Its mass spectrum showed M^+ at m/e 398·39107 ($C_{20}H_{46}N_8$ requires 398·454), and a sample that had been dissolved in D_2O–DCl followed by basification (× 3) showed M^+ at 406, consistent with the presence of eight exchangeable hydrogens and strongly suggesting the coupling of two cyclam moieties by a carbon–carbon bond. This was confirmed by an X-ray structure determination on a dinuclear complex that was obtained by heating a suspension of the amine in an aqueous solution of $Ni(ClO_4)_2{\cdot}6H_2O$ for 6 h. Crystals of the orange product suitable for X-ray analysis were obtained by slow cooling of a hot aqueous solution.‡

Crystal data: $[Ni_2(C_{20}H_{46}N_8)](ClO_4)_4$, monoclinic, space group $C2/c$ $a = 27{\cdot}437(7)$, $b = 9{\cdot}061(2)$, $c = 16{\cdot}927(4)$ Å, $\beta = 120{\cdot}41(2)°$, $Z = 4$. The structure was solved by conventional heavy-atom techniques and refined[5] using 2670 unique data $[F > 3\sigma(F)]$ measured on a Syntex $P2_1$ diffractometer with Mo-$K_{\bar{\alpha}}$ radiation. The final R value

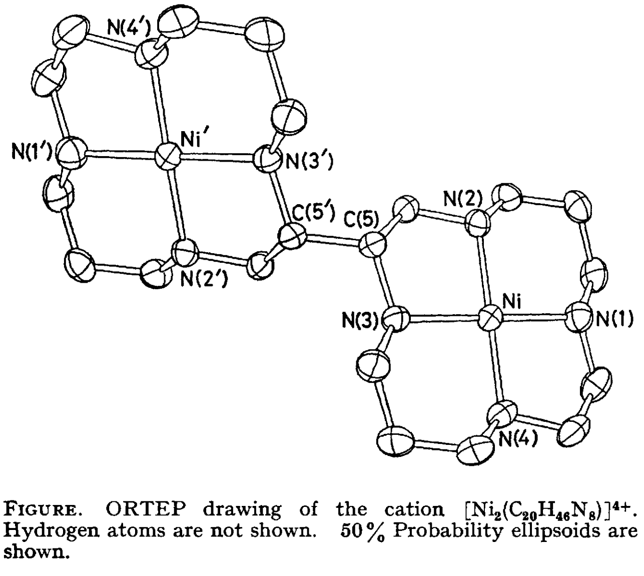
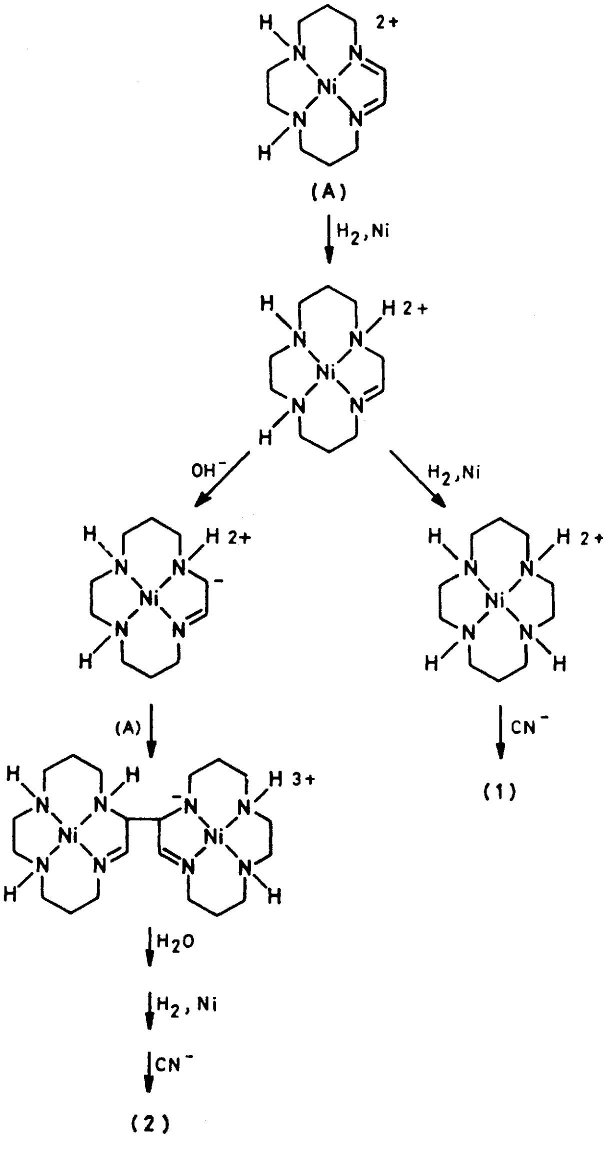


Figure. ORTEP drawing of the cation $[Ni_2(C_{20}H_{46}N_8)]^{4+}$. Hydrogen atoms are not shown. 50% Probability ellipsoids are shown.



Scheme

---

† In contrast to cyclam, the octa-amine is very insoluble in water and most organic solvents. It is soluble in aqueous hydrochloric acid and may be purified by dissolution in acid followed by addition of base (NaOH) to recover the free amine.

‡ Satisfactory elemental analyses were obtained.

for 238 variables is 0·056. In the final cycles of least-squares refinement hydrogen atoms were included in their calculated positions with isotropic thermal parameters; all non-hydrogen atoms were refined anisotropically.§ An ORTEP drawing of the cation is shown in the Figure.¶ The cyclam moieties are connected by a 2,2′-equatorial–equatorial linkage with a normal carbon-carbon distance of 1·542(9) Å. Nickel–nitrogen distances average 1·95(1) Å, which is in the range expected for low-spin planar Ni$^{\mathrm{II}}$–macrocyclic amine distances. Both halves of the complex have the lowest energy, *trans* III,[4] set of donor atom configurations.

A reasonable mechanism for formation of this cation during the cyclization reaction is shown in the Scheme. In support of this sequence we note that ionization of methylene group protons adjacent to an imine in a five-membered ring is well documented[6] as is addition of nucleophiles to co-ordinated imine functions.[3,7] Reductions of co-ordinated α-di-imine functions to mono-imines also have been achieved using hypo-phosphoric acid[8] although no information concerning the mechanism of catalytic reduction is available.

Cyclic voltammetry on the dinuclear complex shows that it undergoes two, quasi-reversible, one-electron oxidations in 0·1 M $[\mathrm{Bu^n{}_4N}][\mathrm{BF_4}]$–acetonitrile at about 0·78 and 0·85 V *vs* the 0·1 M $\mathrm{Ag^+/Ag}$ electrode. This separation is larger than the 36 mV separation expected on a statistical basis;[9] since there is no electronic delocalization, this increased separation is probably a result of electrostatic effects that are expected to favour the 2 [2,3] distribution over the [2,2] + [3,3].[10] A single, irreversible, two-electron reduction occurs at −1·72 V ($i_p^a/i_p^c = 0{\cdot}3$). The formal potentials for $[\mathrm{Ni(cyclam)}]^{2+}$ under the same conditions are 0·67 and −1·70 V.[9]

Like $[\mathrm{Ni(cyclam)}]^{2+}$, the dinuclear complex also exists in aqueous solution as a mixture of four-co-ordinate (planar) and six-co-ordinate species with the equilibrium constant being strongly dependent on ionic strength, although there is a substantial difference in the equilibrium constants. The 460 nm absorption assigned to the four-co-ordinate form of the dinuclear complex has $\epsilon = 26$ l mol^{-1} cm^{-1} (4×10^{-3} M, 21 °C) but in 2·5 M $\mathrm{NaClO_4}$ (the highest concentration that could be utilized) it increases to 110 l mol^{-1} cm^{-1}. This requires that there be $\leqslant 24\%$ of the four-co-ordinate form in water whereas $[\mathrm{Ni(cyclam)}]^{2+}$ ($\epsilon = 64{\cdot}5$ l mol^{-1} cm^{-1} in 6 M NaCl) is about 70% planar under the same conditions.

We thank a referee for helpful comments.

(*Received*, 26*th November* 1980; *Com.* 1265.)

---

§ Oxygen atoms of the perchlorate ions were severely disordered; one ion was refined with five oxygen atoms, two of these with unit occupancy and three at 0·667 occupancy each.

¶ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] E. K. Barefield, *Inorg. Chem.*, 1972, **11**, 2273.
[2] E. K. Barefield, F. Wagner, A. W. Herlinger, and A. R. Dahl, *Inorg. Synth.*, 1975, **16**, 220.
[3] E. K. Barefield, F. Wagner, and K. D. Hodges, *Inorg. Chem.*, 1976, **15**, 1370.
[4] B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 1965, **4**, 1102.
[5] SHELX-76, G. Sheldrick, *X*-Ray System Report, University Chemical Laboratory, Cambridge, 1976.
[6] V. L. Goedken and D. H. Busch, *Inorg. Chem.*, 1971, **10**, 2679.
[7] L. T. Taylor, F. L. Urbach, and D. H. Busch, *J. Am. Chem. Soc.*, 1969, **91**, 1072.
[8] A. M. Tait and D. H. Busch, *Inorg. Chem.*, 1977, **16**, 966.
[9] J. B. Flanagan, S. Margel, A. J. Bard, and F. C. Anson, *J. Am. Chem. Soc.*, 1978, **100**, 4248.
[10] J. E. Sutton, P. M. Sutton, and H. Taube, *Inorg. Chem.*, 1979, **18**, 1017.
[11] F. V. Lovecchio, E. S. Gore, and D. H. Busch, *J. Am. Chem. Soc.*, 1974, **96**, 3109.
[12] A. Anichini, L. Fabbrizzi, P. Paoletti, and R. M. Clay, *Inorg. Chim. Acta*, 1977, **24**, L21.

Printed by Heffers Printers Ltd Cambridge England