3-PF_6 (coordinated form), 63412-99-7; **4**, 63448-96-4; **4** (coordinated form), 63413-00-3; **5**, 63448-98-6; **5** (coordinated form), 63412-97-5; dihydrobis(trimethylamine)boron chloride, 18517-67-4; methylene chloride, 75-09-2.

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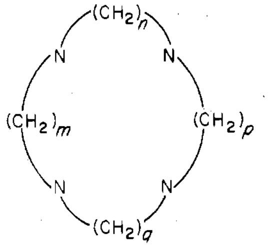
Correspondence

Coplanar Coordination of the Smallest Tetraaza Macrocycle: Low-Spin 1,4,7,10-Tetraazacyclododecanenickel(II)

AIC70230B

Sir:

Selectivity of macrocyclic ligands toward metal ions depends on (i) the effective fitting of the cation into the macrocyclic hole and (ii) the ligand's ability to adjust itself to the electronic and geometrical requirements of the metal. In the case of tetraaza macrocycles, the synthetic availability[1] of 12- to 16-membered ligands has made it possible to consider the superimposing effects of i and ii on the stereochemistry, thermodynamic stability, ligand field parameters, etc., of 3d metal macrocyclic complexes.



$m = n = p = q = 2$	$[12]aneN_4$
$m = n = p = 2; q = 3$	$[13]aneN_4$
$m = p = 2; n = q = 3$	$[14]aneN_4$
$m = 2; n = p = q = 3$	$[15]aneN_4$
$m = n = p = q = 3$	$[16]aneN_4$

For the Co(III),[2] Ni(II),[2] and Fe(II)[3] with most of the above ligands, a tetragonal stereochemistry, with the four nitrogen atoms occupying the equatorial sites, is the most common. Calculations have been made[2] in order to evaluate the conformational energy which a macrocycle expends in arranging its donor atoms at the corners of a square; $[14]aneN_4$ was found to have the least strain, the ideal M–N distance being 2.07 Å. In the case of nickel(II) complexes, the strongest metal–nitrogen interaction, measured as Dq_{xy}, has been found with $[14]aneN_4$,[2] in which the x-ray determined Ni–N distance is 2.06 Å[4] and is closest to the theoretical one. Furthermore, it has been recently shown that for copper(II) (Cu–N distance guessed from analogous tetragonal copper polyamine complexes: 2.01–2.09 Å)[5] the strongest in-plane interaction, as measured from the energy of the d–d band,[6] is evident with $[14]aneN_4$, and this correlates well with the large negative enthalpy of complex formation in water (the most exothermic among complexes with both cyclic and open tetramines).[7]

As the macrocyclic ligand hole becomes smaller, coplanar chelation becomes more and more difficult. The smallest macrocycle $[12]aneN_4$ (or 1,4,7,10-tetraazacyclododecane) has not been found, thus far, to coordinate Co(III) in a planar fashion, but it folds around the metal ion producing a cis complex.[8] In aqueous solution *cis*-(diaquo)$Co([12]aneN_4)^{3+}$ does not isomerize to the *trans*-diaquo species,[9] as, for instance, $Co([14]aneN_4)^{3+}$ does.[10]

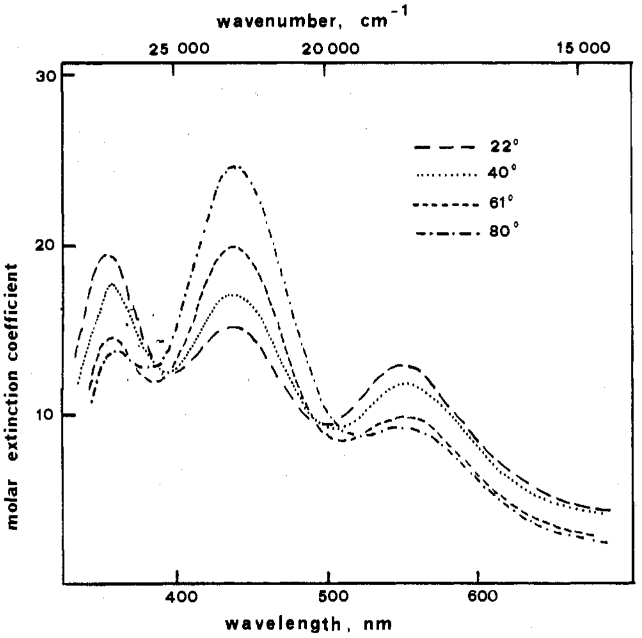


Figure 1. The visible absorption spectra of $Ni([12]aneN_4)^{2+}$ in aqueous 6 M $NaClO_4$, recorded at different temperatures.

An aqueous solution of $Ni([12]aneN_4)^{2+}$ is blue and its electronic spectrum is typical of a high-spin octahedral complex, which is presumably *cis*-diaquo. However, on addition of large amounts of inert electrolyte (e.g., $NaClO_4$) the solution turns brownish. Furthermore, if the solution is heated to boiling, its color becomes bright yellow. An increase in either salt concentration or temperature increases the intensity of a new absorption band at 23 000 cm^{-1}. The intensities of the other bands simultaneously decrease. The electronic spectra of $Ni([12]aneN_4)^{2+}$ in 6 M $NaClO_4$, recorded at different temperatures, are reported in Figure 1.

The absorption band at 21 000–23 000 cm^{-1} is typical of a yellow diamagnetic nickel(II) complex, these properties resulting from a *coplanar* arrangement of the four nitrogen atoms.[11] On the other hand, it is well known that the blue-to-yellow interconversion (1) is strongly favored by ionic strength and temperature.[12]

$$\underset{\text{blue, high spin}}{[NiL(H_2O)_2]^{2+}} \rightleftarrows \underset{\text{yellow, low spin}}{[NiL]^{2+}} + 2H_2O \tag{1}$$

We have demonstrated that *the smallest macrocyclic ligand* $[12]aneN_4$ *is able to reach a* (more or less distorted)

Table I. Energy of the d-d Band for Low-Spin Square-Planar $Ni(tetramine)^{2+}$ Complexes, in Aqueous Solution

Ligand	ν(d-d), cm^{-1}	Ligand	ν(d-d), cm^{-1}
[12]aneN_4	23 260	2,2,2-tet	22 500
[14]aneN_4	22 470	2,3,2-tet	22 420
[15]aneN_4	21 510	3,2,3-tet	21 740
		3,3,3-tet	21 050

square-coplanar stereochemistry, as required in order to stabilize the singlet state of nickel(II) ion.

The impossibility of reaching 100% of the yellow species and determining its limiting spectrum prevents us from making a thermodynamic assessment of the blue-to-yellow equilibrium for [12]aneN_4 complexes at a fixed ionic strength. However, taking a value of 65 ± 15 for the molar extinction coefficient of $Ni([12]aneN_4)^{2+}$, yellow, as presumed from analogous complexes with cyclic and open tetramines,[13] it can be calculated that at 22 °C in 6 M $NaClO_4$ $Ni([12]aneN_4)^{2+}$ exists as 19 ± 6% in the yellow planar form, which becomes 37 ± 10% at 80 °C. On the other hand the room temperature guessed percentage of low-spin $Ni([12]aneN_4)^{2+}$ at lower salt concentration is 9 ± 2 (3 M $NaClO_4$), less than 1% in pure water. It must be noticed that the formation of the yellow species is much more favored with other tetramines (for instance, in 6 M $NaClO_4$, [14]aneN_4 and 2,3,2-tet[14] complexes exist as 100% of the yellow form; $Ni(2,2,2\text{-tet})^{2+}$ as about 70%). The so-called "blue" species in eq 1 must be potentially considered as a mixture of cis α, cis β, and trans octahedral forms,[15] depending upon the nature of L, their quantities being regulated by equilibrium constants for the individual reactions, which makes the interpretation of the equilibrium constant for eq 1 complicated.

In any case, the existence of a square-coplanar $Ni([12]aneN_4)^{2+}$ fits quite well with previous theoretical considerations on the arrangement of macrocyclic ligands around metal ions.[2] The recommended metal-nitrogen distance for [12]aneN_4 in its minimized strain square configuration is 1.83 Å. Low-spin nickel(II) ion in various polyamine complexes exhibits Ni-N distances of 1.90-1.91 Å[16a,17] and the reduced size of low-spin Ni(II) should allow easier fitting of the macrocyclic hole. Therefore, coplanar chelation of [12]aneN_4 is promoted by the small size of Ni(II) together with its strong preference for square coordination. These two properties make low-spin Ni(II) unique among the 3d metal ions. The difficulty in obtaining the yellow low-spin complex, in comparison with other cyclic and open-chain tetramines, which is expressed by the low constant for eq 1, probably reflects the large steric energy spent by [12]aneN_4 on changing from a cis to a trans configuration.

In Table I the energy of the visible band of $Ni([12]aneN_4)^{2+}$, yellow, is compared with that of complexes of upper homologues [14]aneN_4 and [15]aneN_4 and of some complexes of open-chain tetramines. The band energy for the low-spin Ni(II) tetragonal chromophore furnishes a measure of the in-plane metal-donor interaction.[11] It is seen that *the smallest macrocycle [12]aneN_4 exerts the strongest perturbation* and presumably forms the most exothermic bonds, among all the ligands under consideration. Similarly, for open ligands, increasing the size of chelate rings causes a decrease of the in-plane interaction. The effect of mechanical constraints of the ligand on the metal-donor interaction energy has been predicted.[2,18] [12]aneN_4 is the most appropriate ligand to establish strong local interactions with the low-spin nickel(II) ion as it offers its donor atoms at the most appropriate distance and in the most favorable positions (the corners of a square).

Registry No. $Ni([12]aneN_4)^{2+}$, 56647-83-7; $Ni([14]aneN_4)^{2+}$, 46365-93-9; $Ni([15]aneN_4)^{2+}$, 53277-08-0; $Ni(2,2,2\text{-tet})^{2+}$, 24653-01-8; $Ni(2,3,2\text{-tet})^{2+}$, 25669-75-4; $Ni(3,2,3\text{-tet})^{2+}$, 63528-06-3; $Ni(3,3,3\text{-tet})^{2+}$, 35821-92-2.

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Istituto di Chimica Generale
e Inorganica dell'Università
e Laboratorio CNR
50132 Florence, Italy

Luigi Fabbrizzi

Received March 25, 1977

Existence of Direct Metal-to-Metal Bonds in Dichromium Tetracarboxylates

AIC703975

Sir:

Since 1964 when the existence of quadruple bonds between transition metal atoms was first recognized[1] several hundred papers dealing with these and closely related multiple bonds between metal atoms have appeared.[2] Such bonds are best known between pairs of molybdenum atoms and pairs of rhenium atoms, though Tc-Tc, W-W,[3,4] and Cr-Cr bonds of order >3 are also well characterized. With respect to chromium, the proposal of quadruple bonds in the $Cr_2(CH_3)_8{}^{4-}$ ion[2] (d_{CrCr} = 1.980 (5) Å) and in $Cr_2(C_3H_5)_4$[2] (d_{CrCr} = 1.97 Å) has not been disputed. Also in $CrMo(O_2CCH_3)_4$[5] (d_{CrMo} = 2.050 (1) Å) the existence of such a bond is not controversial. There has, however, been some controversy about the electronic structures of substances with the general formula $Cr_2(O_2CR_4)\cdot 2L$ and the general structure **1**, which has D_{4h} symmetry.

The first such compound (R = CH_3; L = H_2O) was discovered in 1844 and a host of others have since been reported. They are all atypical of Cr^{II} compounds generally in being red and essentially diamagnetic rather than blue and paramagnetic. Only in 1970 was one of these compounds correctly characterized structurally[6] at which time it was specifically proposed that a "strong bond exists between the metal atoms", since the Cr-Cr distance was found to be 2.361 (1) Å. We have since shown[7] that in anhydrous $Cr_2(O_2CCH_3)_4$ the metal-metal distance is even shorter, viz., 2.288 (2) Å, al-