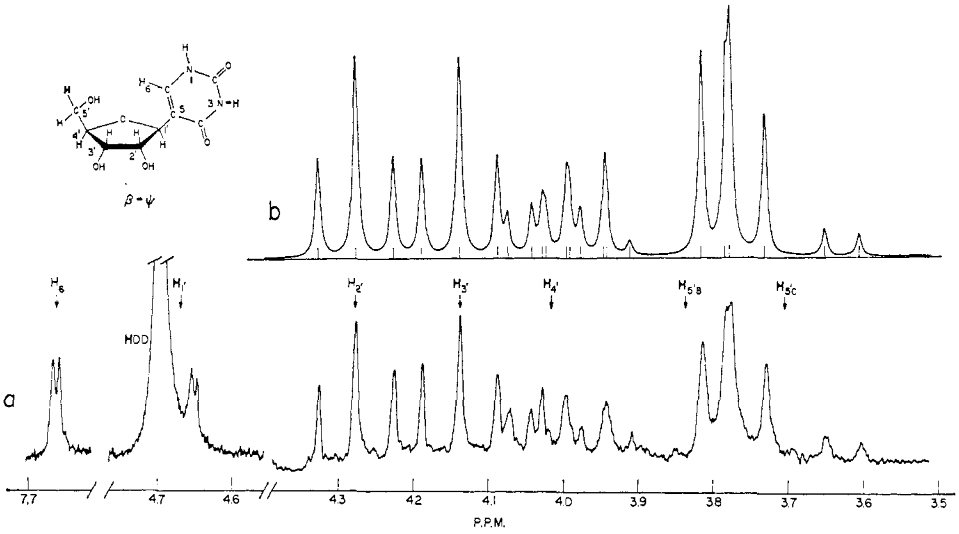

Figure 1. (a) 100-MHz spectrum of $\beta\psi$ in D_2O (pD 6.7, 0.12 M, 30°). Chemical shifts are relative to internal 3-(trimethylsilyl)propanesulfonic acid. A second doublet of the quartet due to H_1' is obscured by the HDO resonance. (b) Simulated 100-MHz nmr spectrum of the region due to ribose protons 2'–5'.

conformations; until now a fixed conformation has been assumed.

(iii) The similarity of the 2' through 5' chemical shifts for $\beta\psi$ and uridine (U) in Table I suggests that the spatial orientations of the uracils relative to the furanose rings are similar. There is evidence that U exists as the *anti* conformer with H_6 above the ring;[10,11] we infer that $\beta\psi$ has the analogous conformation, in agreement with the interpretation of ORD data.[11]

Table II. Measured Dihedral Angles (ϕ) and Calculated J's for Various Furanose Ring Conformations

Atom out of plane[a]	$\phi_{1'2'}$, °	$J_{1'2'}$[b]	$\phi_{2'3'}$, °	$J_{2'3'}$[b]	$\phi_{3'4'}$, °	$J_{3'4'}$[b]
C_2'-*endo*	165	9.5	45	4.3	105	0.4
C_3'-*exo*	145	6.7	40	5.0	100	0
H_2', H_3' eclipsed	120	2.3	0	9.0	120	2.3
C_3'-*endo*	105	0.4	45	4.3	165	9.5
C_2'-*exo*	100	0	40	5.0	145	6.7

[a] *endo* means the atom is located on the same side of the plane defined by $C_1'O_1'$ and C_4' as the C_4'–C_5' bond. *exo* means that it is found on the opposite side. [b] In hertz.

The allylic coupling between hydrogens at position 6 and 1' depends upon the dihedral angle between the planes containing the coupled protons, and thus should be sensitive to the torsional angle between the base and ribose moieties. The constancy of this coupling, the ribose hydrogen couplings, and the ribose hydrogen chemical shifts over a 40° range demonstrates a lack of temperature-induced conformational change. Temperature-independent spectra for three cases have been distinguished;[12] two of these are applicable here. The energy difference between the *syn* and *anti* isomers of nucleosides has been predicted to be large.[13] Thus, a minimal dependence of $J_{6,1'}$ on temperature is expected. In a second case, where energy differences are small, such as rotational isomers of serine,[14] temperature changes do not alter the relative isomer populations appreciably. This applies to the rotamers about the $C_{4'}$–$C_{5'}$ bond, as well as to the ribose ring conformers.

T°C	P_I	P_{II}	P_{III}
30	0.53	0.32	0.15
70	0.47	0.35	0.18

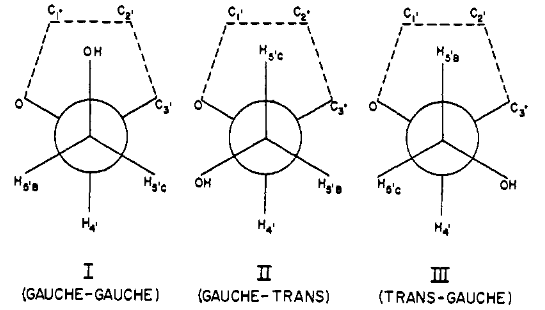

Figure 2. Possible rotational isomers around the C_4'–C_5' bond for $\beta\psi$. The relative populations of these isomers at 30 and 70° are shown above the structures.

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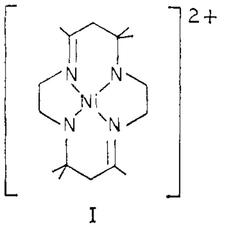
A New and Simple Template Synthesis of Uninegative, Macrocyclic, Corrin-Type Ligands

Sir:

The utility of the coordination template effect in synthesizing macrocyclic, polydentate ligands is well known.[1] The majority of ligands prepared in this manner belong to two classes: (1) ligands which have no charge, or (2) ligands which have a double negative charge. Typical examples of macrocyclic, tetradentate complexes with class 1 and class 2 nitrogen ligands are, respectively, the tetraazadienes of Curtis,[2] structure I, and the tetraazaannulenes of Jäger,[3] structure II. Many related complexes have been prepared using these same procedures.



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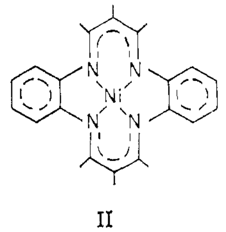
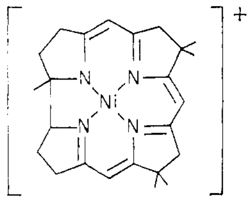
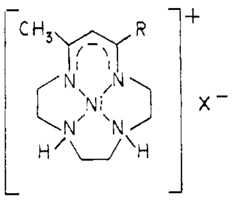


II

Until now, no general method had been found for synthesis of complexes containing the third class of macrocyclic ligands, *i.e.*, ligands which have a single negative charge. In fact, very few such compounds have ever been prepared—these include the partially delocalized nickel–corrin complex, synthesized by the elegant scheme of Eschenmoser,[4] structure III, and various oxime esters.[5-9] Because of the biological importance of corrin ring compounds, a simple and general method for the synthesis of ligands of this type is highly desirable.



III



IV

AT, R = CH_3
TAT, R = CF_3
X = Br^-, I^-, SCN^-, NO_3^-, BF_4^-, and PF_6^-

We now report the template synthesis of two series of nickel(II) complexes, Ni(AT)X and Ni(TAT)X, structure IV, containing the uninegative, partially delocalized, macrocyclic, Schiff base ligands, 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-diene (AT), and 11-methyl-13-(trifluoromethyl)-1,4,7,10-tetraazacyclotrideca-10,12-diene (TAT).[10]

Preparation of Ni(AT)X and Ni(TAT)X has been achieved by two methods which are illustrated for the synthesis of Ni(AT)I. Method A first requires preparation of the linear, sexadentate ligand, bis(acetylacetone)triethylenetetramine, H_2(BAT), by the extension of standard procedures.[11] A 2.1-g sample of H_2(BAT) was dissolved in 25 ml of water which had been adjusted to pH 5 with acetic acid. After the ligand solution had started to reflux, an aqueous solution containing 2.5 g of $Ni(OAc)_2 \cdot 4H_2O$ was added. Refluxing was continued for 6 hr. The hot reaction solution was then filtered into a concentrated aqueous solution of NaI and the pH of the resulting solution was adjusted to 10 with aqueous NaOH. Chilling of the solution resulted in formation of crystals of Ni(AT)I. Method B is an *in situ* reaction,[12] and involves the sequential addition of 1.5 g of triethylenetetramine (trien), acetic acid (enough to adjust the pH of the solution to 5), and 2.0 g of acetylacetone, to a refluxing aqueous solution containing 2.5 g of $Ni(OAc)_2 \cdot 4H_2O$. The solution was refluxed for 6 hr and treated with NaI and base, as outlined in method A. Cooling induced crystallization of Ni(AT)I. In both methods, the yield of Ni(AT)I averaged 30%. Other derivatives can be prepared simply by addition of the required sodium salt in place of NaI.

These same procedures have been employed in the synthesis of the corresponding TAT complexes by using bis(trifluoroacetylacetone)triethylenetetramine,[11] H_2(BTAT), as the sexadentate ligand in method A, and trifluoroacetylacetone as the β-diketone in method B. In addition, complexes of Ni(TAT)X have been prepared by a third technique, method C, which involves rearrangement of the neutral nickel(II) complex, Ni(BTAT).[13] For example: 0.5 g of Ni(BTAT) was refluxed for 6 hr in 25 ml of water which had been acidified to pH 5 with acetic acid. Concentration of the reaction solution, after the usual addition or NaI and base, produced nearly quantitative yields of Ni(TAT)I.

All of the complexes have been isolated as diamagnetic, red-orange crystalline salts of stoichiometry Ni(AT)X and Ni(TAT)X. Absorption bands in regions of the infrared spectrum attributed to the anions in the NO_3^-, SCN^-, $BF_4,^-$ and PF_6^- derivatives indicate that these anions are not coordinated. All of the derivatives are soluble in water and polar organic solvents, and exhibit molar conductances in the range of uniunivalent electrolytes. The visible spectra of Ni(AT)$^+$ and Ni(TAT)$^+$ measured in aqueous solution show a single absorption at 484 ($\epsilon \sim 128$) and 474 mμ ($\epsilon \sim 150$), respectively. The foregoing evidence is consistent with a singlet ground-state nickel(II) configuration in both solid state and solution.

The cyclic structure of the coordinated ligands has been deduced from analytical data, infrared and mass spectra, and nmr measurements. Elemental analyses indicate the presence of only one β-diketone and one amine moiety per nickel atom. At the same time, the infrared spectra contain no bands attributable to free >C=O or NH_2 groups, suggesting that both terminal amines of trien have undergone condensation with the β-diketone to form a cyclic ligand. The infrared spectra of all of the derivatives contain a strong, sharp band in the 3300–3000 cm^{-1} region, which has been assigned to the stretching vibration of the –NH groups of the

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trien backbone, and a medium intensity band or doublet in the 1550 cm^{-1} region, which has been assigned to the C=N and/or C=C stretching modes. In addition, the highest *m/e* peak in the mass spectra of Ni(AT)Br and Ni(TAT)Br is that due to the (parent ion − HBr).

Typical proton nmr spectra are shown in Table I.

Table I. Nmr Spectra of Ni(AT)NO$_3$ and Ni(TAT)NO$_3$ in CDCl$_3$

Ni(AT)NO$_3$, δ^a	Ni(TAT)NO$_3$, δ^a	Band	Assignment
5.88 (2.3)^b	6.23 (2)^b	Broad singlet	-NH-
4.70 (1.2)	5.20 (1)	Sharp singlet	=CH-
3.13^c (13)	3.12^c (13)	Overlapping multiplets	-CH$_2$-
1.87 (6)	1.93 (3)	Sharp singlet	-CH$_3$

^{a} Measured in ppm downfield from internal TMS at 60 MHz. ^{b} Relative areas are shown in parentheses. ^{c} Center of gravity of complex pattern.

In each case, absence of any resonances which might be assigned to -NH$_2$ protons and the presence of a singlet attributed to the vinyl proton are consistent only with formation of a fully condensed macrocyclic ligand containing one partially delocalized six-membered chelate ring.

The template reactions described here should provide the first general synthetic route to metal complexes containing corrin-type ligands, *i.e.*, macrocyclic, Schiff base ligands with a single, partially delocalized negative charge. General application of these techniques is expected to result in the synthesis of many new complexes of this type, including those containing the backbone of the corrin ring.

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The Lifetime and Quenching Rate Constant for the Lowest Triplet State of Sulfur Dioxide

Sir:

Previous attempts to determine the lifetime of optically excited sulfur dioxide triplet molecules in the gas phase have not been successful.[1] A measurement of this quantity is necessary for the solution of the following important problem related to sulfur dioxide photochemistry. The only available triplet lifetime estimate ($\tau_0 = (7 \pm 1) \times 10^{-3}$ sec), made by Caton and Duncan, was based on an excitation of sulfur dioxide by electric discharge. The lifetime showed no detectable dependence on pressure of sulfur dioxide up to 300 μ. However the rate constant data of Strickler and Howell[2] and Rao, Collier, and Calvert[3] suggest that a significant decrease (from 35 to 75%) should have been observed over the pressure range used by Caton and Duncan.

We wish to report the findings of a study in which we have determined the lifetime of sulfur dioxide triplet species which have been generated in two distinct photochemical ways: (1) direct laser light excitation of sulfur dioxide to the first excited triplet state ($^3SO_2$) by absorption at 3828.8 Å within the "forbidden" triplet ← singlet band; and (2) flash photolytic excitation of sulfur dioxide to the first excited singlet state ($^1SO_2$) with subsequent triplet population by intersystem crossing.

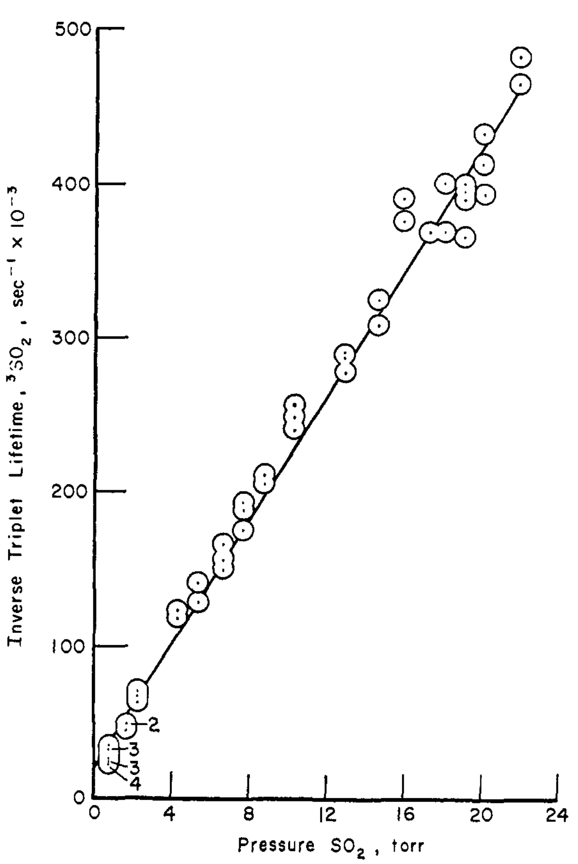

Figure 1. Plot of the inverse sulfur dioxide triplet lifetime *vs.* pressure of sulfur dioxide; data from the laser-excited sulfur dioxide experiments at 3828.8 Å.

The experimental details and the complete results of this study will be published elsewhere. A brief description is given here. The laser pulse of 3828.8-Å wavelength was generated from the output of a 75-MW ruby laser (6943 Å) by Raman shifting (1344 cm^{-1}) using nitrobenzene, followed by frequency doubling. About 50 kW of power at 3828.8 Å resulted in a half-intensity peak duration of 20 nsec. The intensity of phosphorescence emission was monitored at right angles to the excitation beam by a spectrally filtered phototube whose output was traced on an oscilloscope and photographed. For the apparatus employed in this work, pressures of SO$_2$ in the range 1–25 Torr gave signals which were sufficient to allow lifetime estimates with reasonable accuracy. The analog data from both the laser and the flash systems were digitized semiautomatically and reduced using least-squares computer programs. In the laser study, excitation occurred only in reaction I. Triplet decay in this system was by the reactions 1, 2, and 3. The lifetime data from the laser system are summarized in Figure 1.

The flash system employed in the second method was a flash photolysis apparatus with a 6-μsec half-intensity peak width. It was constructed to follow the phosphorescence intensity of the filtered, highly collimated beam

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