preliminary attack on this problem, we have constrained the wave functions of the degenerate states to span the C_{2v} or D_{2h} subgroup of the molecular point group rather than the true molecular point group D_{3h} or D_{6h}, so that we can describe the ground state by a single Slater determinant. In the VO procedure this leads to a splitting of the original degeneracy. One could view this splitting as a precursor to the Jahn–Teller splitting which arises when the molecular geometry is distorted in such a way as to lower the symmetry of the molecule to C_{2v} or D_{2h}. In the SCF procedure this problem does not arise; the two components of the degenerate ground state remain degenerate within the estimated precision of the calculations and, since they span different irreducible representations of the subgroup, are not expected to interact, so that the energy may be accepted.

In benzene and its hexafluoro derivative one sees the *pre-Jahn–Teller splitting* of the degenerate states in the VO approximation. The hexafluorobenzene calculations suggest a somewhat different interpretation of the experimental results than that given by Robin, *et al.*,[15] in that the state at 3.8 eV above the ground state is a nondegenerate B_{1u} σ state and the state at 4.5 eV is the doubly degenerate E_{1g} σ state. In triazine, our calculations support the assignment of the ground state as a doubly degenerate n state and the first excited state as a doubly degenerate π state.[15] In trifluorotriazine, our calculations suggest that these two states have become nearly degenerate. Therefore, the first ionization observed represents ionization to both the n and π states. Such an assignment will lead to a fluorine shift of about 2.0 eV, which is in the expected range.[15] It is interesting to note the large pre-Jahn–Teller splitting we are getting in these two compounds compared to benzene and hexafluorobenzene. This same behavior is observed in the experimental spectra.[15]

We are currently extending this work to larger systems and higher energy states. We are also investigating how the optical spectrum of ions can complement PE methods, since states may be observed in the optical spectrum which have vanishing PE cross sections.

(15) M. B. Robin, N. A. Kuebler, and C. R. Brundle in "Electron Spectroscopy," D. A. Sherly Ed., North-Holland Publishing Co., Amsterdam, 1972, pp 351–377.

R. L. Ellis

Department of Chemistry, University of Illinois
Urbana, Illinois 61801

H. H. Jaffé,* C. A. Masmanidis

Department of Chemistry, University of Cincinnati
*Cincinnati, Ohio 45221*

Preparation of Macrocyclic Tertiary Amine Complexes of Nickel(II) by Alkylation of Coordinated Amine. Crystal Structure of a Monoazide Bridged Dimer of Ni(N-tetramethylcyclam)²⁺

Sir:

Recently we reported the preparations of **1** and some of its metal complexes.[1] A surprising and disappointing property of these complexes was their lability, which was apparently a result of the set of nitrogen donor configurations that was dictated by the kinetic precesses

(1) E. K. Barefield and F. Wagner, *Inorg. Chem.*, 12, 2435 (1973).

leading to complex formation.[2] Spectroscopic data were consistent with a structure which had all four methyl groups on the same side of the coordination plane defined by the four donor nitrogens.[2] However, we expected that a synthesis that involved N-alkylation of **2** (NiCyclam²⁺) might produce a different set of nitrogen donor configurations and, as a result of this, a more inert complex. This reasoning led us to explore procedures for alkylation of the coordinated amines in this complex and the related systems **3** and **4**.

1
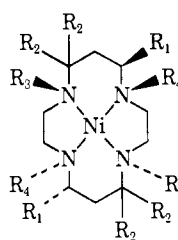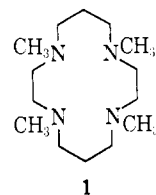
2, R = H
3, $R_1 = R_2 = CH_3$; $R_3 = R_4 = H$
5, $R_1 = R_2 = H$; $R_3 = R_4 = CH_3$
6, $R = CH_3$
8, $R_1 = R_2 = CH_3$; $R_3 = CH_3$; $R_4 = H$
9, $R_1 = R_2 = CH_3$; $R_3 = H$; $R_4 = CH_3$
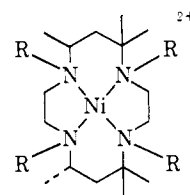
4, R = H
7, R = CH₃

Coordinated amines have no nucleophilic properties; however, removal of a proton generates a nucleophilic amide which may be alkylated.[3] We have found that the base–solvent systems $KOH–DMSO$[4] and $NaCH_2S(O)CH_3–DMSO$[5] are useful for generating deprotonated forms of **2–4** as well as a variety of other macrocyclic amine complexes of nickel(II) and that these deprotonated forms may be alkylated with several reagents. This communication provides a preliminary account of certain aspects of this work including the results of an X-ray structural determination on a Ni(II) complex of **1** that was prepared by N-alkylation of **2**.

Complexes **2–4** react instantaneously with 1 equiv of $NaCH_2S(O)CH_3$ in DMSO to yield highly colored

(2) There are five sets of nitrogen configurations for a coplanar array of nitrogen donors. Schematically these are

B + +   D + –
  + +   + –
C – +   E + +
  + –   + –
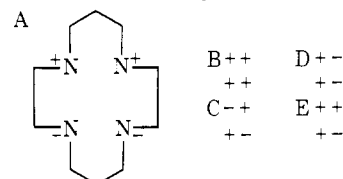
Discussions of stereochemistry in these systems of a general nature are given by B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 4, 1102 (1965). A more detailed analysis is given by L. G. Warner and D. H. Busch, *J. Amer. Chem. Soc.*, 91, 4092 (1969); "Coordination Chemistry: Papers Presented in Honor of J. C. Bailar, Jr.," Plenum Press, New York, N. Y., 1969. The trans-dichloro complex of **2** has the set of nitrogen configurations shown as (A): B. Bosnich, R. Mason, P. Pauling, G. B. Robertson, and M. L. Tobe, *Chem. Commun.*, 97 (1965).

(3) G. W. Watt and P. W. Alexander, *Inorg. Chem.*, 7, 537 (1968), and references cited.

(4) W. L. Jolly, *Inorg. Syn.*, 11, 113 (1968); *J. Chem. Educ.*, 44, 304 (1967).

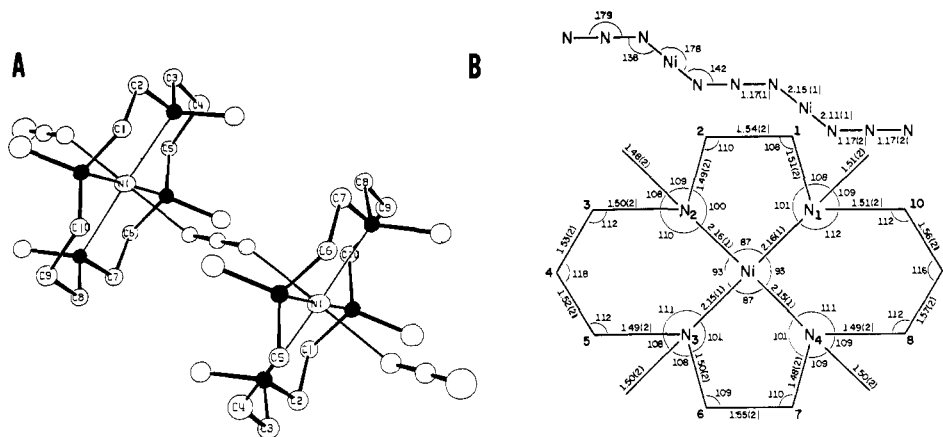(5) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 84, 866 (1962); 87, 1345 (1965).

Figure 1. (A) Projection drawing of $[Ni_2(C_{14}H_{32}N_4)_2(N_3)_3]^+$. Iodide counterion is not shown. Atoms are indicated as 50% probability volumes. (B) Bond distances and angles for complex shown in A.

species (**2**, purple; **3** and **4**, blue). Addition of a second equivalent of base produces red species in each case. Additional base produced no further change. Thus these colored intermediates correspond to mono- and doubly deprotonated forms of the macrocyclic complexes. Red, insoluble materials were produced in reactions of **2–4** with 2 equiv of KNH_2 in liquid ammonia. The stereochemistry of the doubly deprotonated species has not been established but addition of methyl iodide to the doubly deprotonated form of **3** in DMSO yielded a trans-dimethylated complex as the major product after fractional crystallization. This product must be either **8** or **9** since only four types of methyl groups were detected in the pmr spectrum.

Addition of finely divided KOH (*ca.* 6 g) to solutions of **2–4** in DMSO (2 g/35 ml, perchlorate salts) resulted in formation of species identical with those obtained with $CH_3S(O)CH_2^-$ as the base. The first deprotonation was again instantaneous but the second step required *ca.* 1 hr for **3** and **4** and several hours for **2**. Addition of excess methyl iodide any time after KOH addition caused a vigorous, exothermic reaction to occur. After the reaction had ceased, the KOH was removed by filtration. Addition of ethanol (1 vol) and ether (2–3 vol) yielded reddish complexes (**5**, **6**, and **7** from **2**, **3**, and **4**, respectively).[6] Infrared spectra of **4–7** contained no N–H stretching absorptions and their pmr spectra contained resonances that were assigned to N-methyl groups.[7] Formation of tetra-N-alkylated complexes is due to further deprotonations and alkylations of partially alkylated species in the presence of the excess base and methyl iodide. Complexes **5–7** are very inert not only to concentrated acids but also to hot aqueous cyanide, which may be used to remove the ligands from the nickel ion in **2–4**.[8]

A totally unambiguous assignment of the stereo-

chemistry of the tetraalkylated products can not be made on the basis of pmr data alone. It is clear that only one isomer was isolated in each case and the number of methyl resonances found in the pmr spectra of **6** and **7** limits the number of possible stereochemistries. If the same factors that determine the stereochemistry of the thermodynamically most stable forms of complexes **2–4** also determine the stereochemistry of the deprotonated forms, then nucleophilic reactions of the coordinated amide ions should occur with retention (or inversion) of each nitrogen configuration, provided there are no substantial steric interactions between N-alkyl groups and the macrocyclic ring. If these points are correct, then complexes **5–7** should have the cyclam-like structure.[2] The pmr data for **6** and **7** are clearly in agreement with this type of structure.[2]

In order to establish whether or not the above points were valid a structural determination was undertaken on one of the derivatives obtained for **5**. The complex of composition $Ni_2(C_{14}H_{32}N_4)_2(N_3)_3I$ was chosen for this study because the solid-state infrared and electronic absorption spectral data were most consistent with a structure having a bridging ligand. This material crystallizes as blue truncated octahedra upon addition of excess sodium azide to aqueous solutions of the iodide salt of **5**. Crystal data are: $M = 883$; orthorhombic space group $Pbca$; $a = 16.115(9)$, $b = 14.779(7)$, $c = 15.732(8)$ Å; $\rho_{calcd} = 1.56$, $Z = 4$, $\rho_{measd} = 1.54$ g cm^{-3} (CCl_4–hexane). Data were collected on a Picker-FACS-1 automated diffractometer. Crystal decomposition by the X-ray beam (Cu Kα) required the use of three crystals to collect a total of 2638 nonzero reflections ($I > 2\sigma$) to $2\theta = 130°$. Appropriate scaling techniques were used to merge the three data sets, each consisting of approximately 1000 reflections. No absorption corrections were made. The structure was solved using heavy atom methods. After several cycles of least-square refinement, in which only the nickel and iodine atoms were treated anisotropically, the solution refined to $R = 0.110$ ($R_W = 0.128$). A difference Fourier map showed electron density peaks of magnitudes consistent with the hydrogen atoms in the macrocycle, but these were not explicitly included in the refinement. For additional information concerning atomic coordinates and structure factor amplitudes, see paragraph at end of paper regarding supplementary material.

(6) Yields of **6** and **7** were routinely 60–80%. Yields by this method were lower for alkylation of **2** but comparable yields could be obtained by filtering the KOH from the purple solution, then adding methyl iodide and after reaction ceased adding more KOH. After the second addition of KOH further reaction takes place and then the reaction mixture is worked up as before. Complexes are isolated as iodide salts.

(7) Methyl resonance positions (obtained on trifluoroacetic acid solutions at 100 MHz): **5** (N–CH₃) τ 7.10; **6** (C(H)C*H₃*) τ 8.86, doublet, $J = 6$ Hz (half of this doublet is obscured at 100 MHz), (C(CH₃)₂) equatorial 8.82, axial 7.38, (N–CH₃) 7.05, 6.80; **7** (C(H)C*H₃*) 8.86, doublet, $J = 6$ Hz (half of this doublet is obscured at 100 MHz), (C(CH₃)₂) equatorial 8.82, axial 7.20, (N–CH₃) 7.00, 6.80.

(8) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 1 (1968); E. K. Barefield, *Inorg. Chem.*, **11**, 2273 (1972).

A projection view of the structure is shown in Figure 1A and bond distances and angles are shown in 1B. The dimeric cation has a crystallographic center of symmetry coincident with the central nitrogen atom of the bridging azide ion. The set of nitrogen donor configurations is the same as that determined previously for the trans-dichloro complex of 2 and that inferred from pmr studies on 3 and 4.[2] No significant steric interactions involving the methyl groups are apparent. A unique feature of the structure reported here is the single end-to-end azide bridge between the two nickel complex moieties. To our knowledge, an azide bridge of this type has not previously been demonstrated by structural methods.[9] The dimeric cation does not exist as a detectable species in solution. Dissociation to the planar form and to a pentacoordinate form takes place in water and nitromethane, respectively.

The structure determined for 5 is the one having the most favorable set of ring conformations. It seems reasonable to assume that the same set of nitrogen configurations is present in 6 and 7. The extreme inertness of these complexes is due to their resistance toward folding along a N–Ni–N direction which is required as a preliminary step to ligand dissociation.[10] Although kinetic and thermodynamic factors cannot be separated on the basis of the available data, clearly, the complex obtained from 1 and nickel ion has a kinetically controlled stereochemistry and it is probably thermodynamically less stable than 5.

Supplementary Material Available. A listing of atomic coordinates and structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-2625.

(9) U. Müller, *Struct. Bonding (Berlin)*, **14**, 141 (1972); Z. Dori and R. F. Ziolo, *Chem. Rev.*, **73**, 247 (1973). A single azido bridge has been claimed for $M_2(Ph_3P)_4(CO)_2N_3^+$ (M = Rh, Ir) but no structural data are available; K. v. Werner and W. Beck, *Chem. Ber.*, **105**, 3209 (1972).
(10) D. K. Cabbiness and D. W. Margerum, *J. Amer. Chem. Soc.*, **92**, 2151 (1970).

F. Wagner, M. T. Mocella, M. J. D'Aniello, Jr.
A. H.-J. Wang, E. Kent Barefield*

*W. A. Noyes Laboratory, School of Chemical Sciences
University of Illinois
Urbana, Illinois 61801*

Determination of Optical Purity Using Circular Polarization of Luminescence

Sir:

The method of circular dichroism (CD) is based on the property of optically active compounds to absorb left and right circularly polarized light unequally. Both Samoïlov[1] and Emeis and Oosterhoff[2,3] independently showed this phenomenon of CD to have an analog in emission: an optically active molecule in solution[2,3] or an optically active crystal of an optically inactive compound,[1] when excited, may preferentially emit left of right circularly polarized light. Their experiments[1-3] led to the introduction of the method of circular polarization of luminescence (CPL).

The method of CPL has many potential applications.[2,4,5] One of them, the determination of optical purity, has been proposed by Eaton.[6] The suggested procedure[6] requires the measurement of CPL of the mixture of enantiomers of which the optical purity has to be determined and of the corresponding racemic mixture. However, this racemate may not always be at hand, e.g., if the mixture of enantiomers has resulted from the conversion of a natural product. Moreover, the effect in CPL of a racemate might be too small for measurement because it is a factor $0.5g$ smaller than the effect of the corresponding optically pure compound.[4,7] It will be shown that the use of a racemate can be avoided.

Let us consider a homogeneous mixture of enantiomers, L and R, containing n_L molecules of L and n_R molecules of R. L is assumed to be the main component of this mixture. A quantity, p, related to the optical purity ($= 100p(\%)$) can then be introduced

$$p = \frac{n_L - n_R}{n_L + n_R}; \quad (p > 0) \qquad (1)$$

Irradiation of the mixture with left circularly polarized (l) light gives rise to excited-state populations of L and R, n_L^* and n_R^*

$$n_L^* = a_1 n_L$$
$$n_R^* = a_2 n_R \qquad (2)$$

whereas irradiation with right circularly polarized (r) light of the same wavelength and intensity results in

$$n_L^* = a_2 n_L$$
$$n_R^* = a_1 n_R \qquad (3)$$

The coefficient a_1 is proportional to the intensity of the exciting light and to the molar extinction coefficient ϵ_1 pertaining to molecules of L absorbing l-light or to molecules of R absorbing r-light.[9]

The g factor[7] can be expressed in our symbols

$$g = \frac{a_1 - a_2}{1/2(a_1 + a_2)} = \frac{\epsilon_1 - \epsilon_2}{1/2(\epsilon_1 + \epsilon_2)} \qquad (4)$$

If e is defined as the fraction of the intensity of the light emitted by L which is l-light at the wavelength of

(1) B. N. Samoïlov, *Zh. Ekspl. Teor. Fiz.*, **18**, 1030 (1948); *Chem. Abstr.*, **43**, 4138d (1949); see also M. S. Brodin and V. Ya. Reznichenko, *Ukr. Fiz. Zh. (Ukr. Ed.)*, **10**, 178 (1965); *Chem. Abstr.*, **63**, 149c (1965).
(2) C. A. Emeis and L. J. Oosterhoff, *Chem. Phys. Lett.*, **1**, 129 (1967).
(3) C. A. Emeis, Thesis, Leiden, 1968.
(4) H. P. J. M. Dekkers, C. A. Emeis, and L. J. Oosterhoff, *J. Amer. Chem. Soc.*, **91**, 4589 (1969).
(5) A. Gafni and I. Z. Steinberg, *Photochem. Photobiol.*, **15**, 93 (1972).
(6) S. S. Eaton, *Chem. Phys. Lett.*, **8**, 251 (1971).
(7) g has the conventional meaning of the ratio of the effects in CD ($\Delta\epsilon(\lambda)$) and in absorption ($\epsilon(\lambda)$) of the *optically pure* compound.[8]
(8) Irradiation takes place at wavelength λ, measurement of the emission phenomena at wavelength λ'. In order to keep the formulas as simple as possible both λ and λ' have been omitted from (1–10).
(9) (2) and (3) hold only if the Lambert–Beer law is valid.