meter equipped with a Beckman E-2 glass and saturated calomel electrode pair. A Pyrex vessel with an outer jacket was used for the titrations. The temperature of the solvent system was kept constant to within 0.1° by circulating water from a constant-temperature bath through the outer jacket of the titration vessel.

A known excess of perchloric acid was added initially to be certain that all the diamine was present as a diammonium ion, and also to repress the extent of initial chelate formation.

The standard sodium hydroxide was stored in polyethylene bottle and standardized against potassium acid phthalate.

Approximately 0.01 M stock solutions of metal ions were prepared by dissolving the metal perchlorate, obtained from G. F. Smith Co., in water. The copper(II) solution was standardized by titration with a standard solution of disodium ethylenediaminetetraacetic acid (EDTA) using 1-(2-pyridylazo)-2-naphthol (PAN) as indicator.[24] The nickel(II) solution was standardized by back-titration of its EDTA complex with standard copper solution and PAN as indicator.[24]

(24) H. A. Flaschka, "EDTA Titrations," Pergamon Press, New York, N. Y., 1959, p 81.

Contribution from the Evans Chemical Laboratory, The Ohio State University, Columbus, Ohio 43210, and the Department of Chemistry, University of Washington, Seattle, Washington

Some Tetragonal Cobalt(III) Complexes Containing Tetradentate Macrocyclic Amine Ligands with Different Degrees of Unsaturation

By SUSAN C. JACKELS, KEITH FARMERY, E. KENT BAREFIELD, NORMAN J. ROSE, and DARYLE H. BUSCH*

Condensation reactions under highly specific conditions have yielded series of cobalt complexes with two new macrocyclic ligands that vary in the extent of their unsaturation, and hydrogenation has given a related series of derivatives of a fully saturated ligand. All are 14-membered macrocycles containing four nitrogen donors; TIM has 4 imine groups; DIM, 2 imines and 2 secondary amines; and DMC, 4 amines. The syntheses, structures, and properties of the resulting series of cobalt(III) complexes, trans-[Co(TIM)X₂]Y, trans-[Co(DIM)X₂]Y, and trans-[Co(DMC)X₂]Y, are reported for X⁻ = halide or NO₂⁻ and Y⁻ = halide, ClO₄⁻, or PF₆⁻. Infrared and pmr spectral studies provide proof of the structures of the macrocyclic ligands in these compounds and the latter has given insight into stereochemical relationships among these complexes. Spectrochemical studies reveal that the ligand field strengths of the macrocycles increase as the degree of unsaturation of the ligand increases. Comparisons with other macrocycles show the relative effect on ligand field strengths of such groups as –N(H)–, N=C, –N=C––C=N–, and py. Voltametric data show clearly that the lower oxidation states of cobalt are stabilized by greater degrees of ligand unsaturation.

Introduction

Because of their physical and chemical properties, cobalt(III) complexes are convenient vehicles for the study of the various subtle stereochemical and electronic relationships that accompany the formation of macrocyclic complexes.[1,2] These include formation of cis and trans isomers by the same macrocycle in octahedral complexes (cis and trans referring to the positions of the fifth and sixth ligating groups), the optical activity of coordinated amine functions, possible enhanced ligand field strength because of mechanical constrictive effects, the relationship between ligand field strength and extent and arrangement of ligand unsaturation, special rate effects, and the energetics and consequences of various chelate ring conformations. Early stereochemical studies suggest that most macrocyclic ligands, especially 14-membered ones, favor

formation of either the *cis*- or *trans*-diacidotetramine isomers. While the majority of the ligands, *e.g.*, those of structures I–III, appear to favor the trans structure with monodentate extracyclic ligands,[3–6] all can be forced into folded forms to produce cis structures with bidentate extracyclic ligands (C₂O₄²⁻, acac). Perhaps the general preference for the planar structure is related to the action of such restrictive factors as steric interactions of methyl groups in the folded form[7] or inflexibility of unsaturated structures (1,7-CT and others). The fact that the unsubstituted 14-membered ring cyclam will form the cis structure[4] with monodentate ligands supports this point of view. *meso*-CRH (structure IV) readily forms cis and trans isomers.[7] If a flexible ring is too small to encompass

cyclam   1,7-CTH   1,7-CT

I   II   III

meso-CRH   cyclen

IV   V
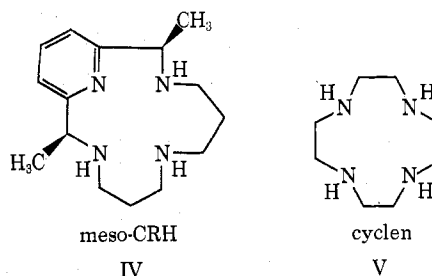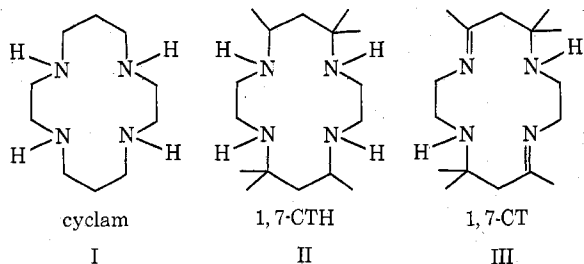
(1) L. F. Lindoy and D. H. Busch, *Prep. Inorg. React.*, **6**, 1 (1971), and references therein.

(2) D. H. Busch, V. Goedken, V. Katovic, A. C. Melnyk, C. R. Sperati, and N. E. Tokel, *Advan. Chem. Ser.*, **No. 100** (1971), and references therein.

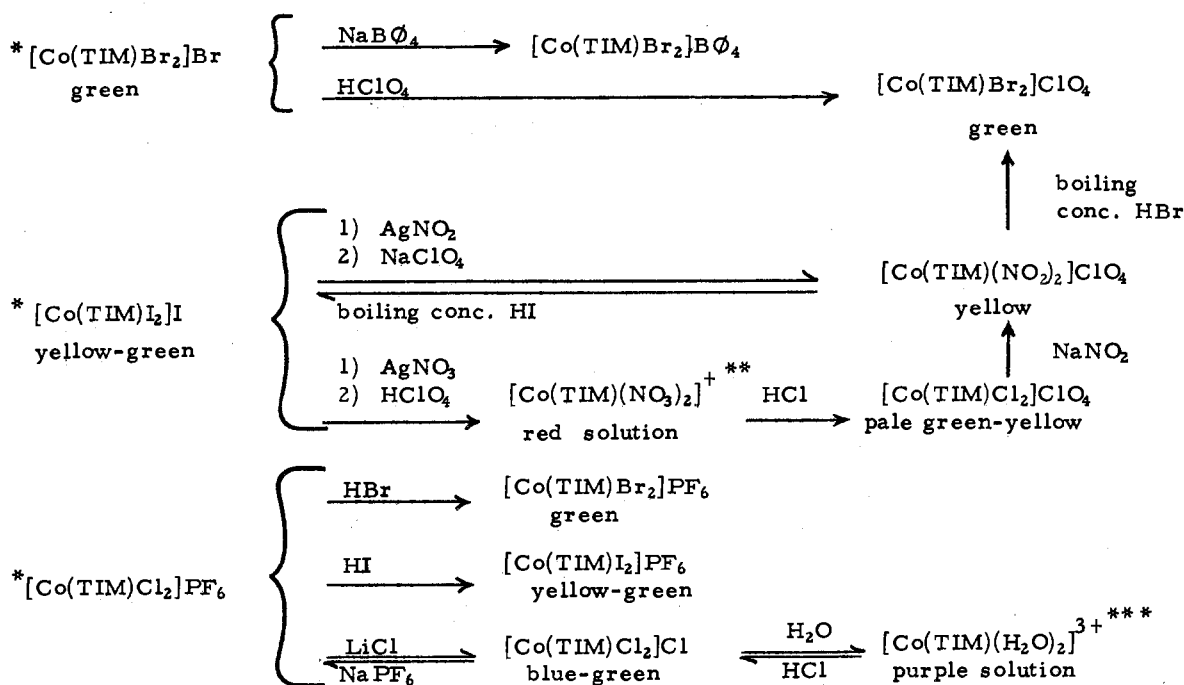(3) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).

(4) C. K. Poon and M. L. Tobe, *J. Chem. Soc. A*, 1549 (1968).

(5) B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, **4**, 1102 (1965).

(6) N. Sadasivan, J. A. Kernohan, and J. F. Endicott, *ibid.*, **6**, 770 (1967).

(7) E. Ochiai and D. H. Busch, *ibid.*, **8**, 1474 (1969).

(8) J. P. Collman and P. W. Schneider, *ibid.*, **5**, 1380 (1966).

* obtained directly from original reaction mixture (see Experimental).
** not isolated, solution contains paramagnetic material and may be a mixture of aquo and nitrato complexes.
*** not isolated, solution contains paramagnetic material and may be a mixture of aquo and chloro complexes.

Figure 1.—Metathetical relationships among [Co(TIM)X₂]Y complexes.

the metal ion, it may serve as a tetradentate chelate only in folded form as found for the case of cyclen (structure V).[8] In the cases of inflexible ligands, such as the highly unsaturated porphyrin ring, metal ions that are too large are simply displaced out of the planar ring.

In our experimental explorations on the complexes of cobalt(III) with 14-membered macrocyclic ligands we vary the degree of unsaturation and look for stereochemical and electronic manifestations of the sorts of phenomena described above. As the degree of unsaturation increases, ligand field strength is expected to increase. This expectation follows first from the fact that imines are stronger donors toward Co(III) than are secondary amines but also from the fact that the metal ion site in the ring is made smaller as the extent of unsaturation increases. An inverse trend would suggest that the metal ion had been forced out of the plane because the ring became too small to encompass it.

We have embarked on a systematic study of the
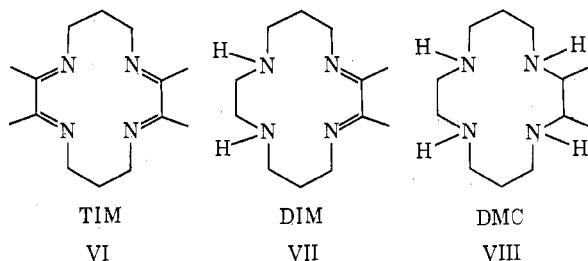
relationships between structural parameters, chemical and physical properties of the complexes, and the susceptibility to synthesis, stability, and reactivity of Co–C-bonded derivatives. The compounds reported here play a central role in that study.[9]

In order to produce ligands having structures VI–VIII we have adapted Baldwin and Rose's synthesis of Ni(TIM)²⁺ salts[10] to the preparation of the cobalt(III) complexes. TIM is a ligand containing two conjugated α-diimine groupings, the closely related DIM has a single conjugated α-diimine grouping, and DMC is fully saturated. The complexes to be described are [Co(TIM)X₂]Y, [Co(DIM)X₂]Y, and [Co(DMC)X₂]Y (TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; DIM = 2,3-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,3-diene; DMC = 2,3-dimethylcyclam; X⁻ = halide or NO₂⁻; Y⁻ = halide, PF₆⁻, or ClO₄⁻). All three ligands belong to the family of 14-membered rings that may be regarded as derived from cyclam I by substitution of methyls for hydrogens and by dehydrogenation. The ligands first reported by Curtis[3] (II, III, and their isomers) also belong to this class. TIM and DIM are the first macrocyclic ligands containing the α-diimine groupings to be coordinated to cobalt and TIM is the first cyclic tetraimine to be coordinated to that metal.

(9) We have recently disclosed the existence of three different classes of Co–C σ-bonded compounds with derivatives of TIM: K. Farmery and D. H. Busch, *Chem. Commun.*, 1041 (1970).

(10) D. A. Baldwin and N. J. Rose, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, No. INOR 20.

TIM   DIM   DMC

VI   VII   VIII

TABLE I

ANALYTICAL DATA FOR THE COMPLEXES

		Found				Calcd			
Complex	Color	C	H	N	Hal	C	H	N	Hal
[Co(TIM)Cl₂]ClO₄	Gray-green	35.16	5.13	12.34	22.10	35.20	5.06	11.73	22.27
[Co(TIM)Cl₂]PF₆	Blue-green	32.28	4.79	10.41	13.44	32.14	4.62	10.36	13.56
[Co(TIM)Br₂]PF₆	Green	27.63	3.76	9.07	25.99	27.47	3.95	9.15	26.11
[Co(TIM)Br₂]Br	Green	30.72	4.46	10.40	43.56	30.74	4.42	10.24	43.83
[Co(TIM)Br₂]ClO₄	Green	29.96	4.26	9.40	28.47	29.68	4.27	9.89	28.21 (Br)
[Co(TIM)I₂]I	Green-brown	24.60	3.44	8.08	55.39	24.44	3.52	8.14	55.34
[Co(TIM)(NO₂)₂]ClO₄	Yellow	33.70	4.81	16.83	7.12	33.71	4.85	16.85	7.11
[Co(DIM)Cl₂]ClO₄	Deep green	31.81	5.33	12.08	23.25	31.77	5.33	12.35	23.45
[Co(DIM)Br₂]ClO₄	Bright green	26.50	4.48	10.15	29.28	26.60	4.47	10.34	29.50 (Br)
[Co(DIM)Br₂]PF₆	Bright green	24.91	4.28	10.04	28.26	24.51	4.11	9.53	27.18 (Br)
[Co(DIM)(NO₂)₂]ClO₄	Yellow	30.09	5.00	17.20	7.63	30.36	5.10	17.70	7.47
[Co(DMC)Cl₂]ClO₄	Apple green	31.70	6.17	11.67	23.59	31.49	6.17	12.24	23.24
[Co(DMC)Br₂]ClO₄	Green	26.59	4.79		29.69	26.37	5.16	10.25	29.24 (Br)
[Co(DMC)(NO₂)₂]ClO₄	Yellow-orange	29.97	5.99	17.38	7.71	30.10	5.89	17.55	7.41

Results and Discussion

Cobalt Complexes of TIM.—The cobalt complexes of TIM were prepared by first mixing biacetyl with the primary diamine 1,3-diaminopropane (TMD), in the presence of 1 equiv of hydrogen ion, followed by the addition of cobalt(II) acetate to the mixture. Experiments designed to test the dependence of yield on variables strongly indicate that the presence of H⁺ ion determines whether or not a macrocyclic complex forms and that, given the presence of H⁺, the time at which the cobaltous ions are added to the reaction mixture influences the yield of the macrocyclic complex. The procedures in the Experimental Section use the optimized conditions. Substitution of Ni(II)[10] or Fe(II)[11] for Co(II) in the procedure given results in the synthesis of the corresponding metal–TIM complex. These observations are consistent with a reaction course in which a specific acid-induced intermediate, or perhaps the organic macrocycle itself, is formed prior to the point in the mechanism where the metal ion plays a role. We have been unsuccessful in our limited attempts to prepare the salts of the free organic macrocycle. While the dihalo complexes are conveniently synthesized directly from cobalt(II) and the ligand precursors, a number of other complexes can be prepared by metathetical methods (Figure 1). Analytical data appear in Table I.

The infrared spectrum of [Co(TIM)Cl₂]PF₆ shows a very close correspondence to that of [Ni(TIM)]-(PF₆)₂[10,12] in the 4000–400-cm⁻¹ region and there are no bands present that could be assignable to either a C=O or NH₂ functional group. This confirms the macrocyclic structure of the ligand. The band found in the range from 1550 to 1600 cm⁻¹ is assigned to $\nu(CN)_{sym}$ while the very weak band at 1640 cm⁻¹ is attributed to $\nu(C=N)_{asym}$. A sharp band at ∼1210 cm⁻¹ is also characteristic of complexes of this ligand.

The results of conductivity studies verify that, except for [Co(TIM)I₂]I, all the TIM complexes reported here are essentially 1:1 electrolytes in methanol (Λ_M varying between ∼100 and 120 ohm⁻¹ M⁻¹ cm² for solutions 10⁻³–10⁻⁵ M) and acetonitrile (Λ_M being ∼155 ohm⁻¹ M⁻¹ cm² for a 10⁻³ M solution of [Co-

(TIM)Cl₂](PF₆)).[13,14] In the case of [Co(TIM)I₂]I rapid dissociation of one coordinated iodide occurs at concentrations below 2 × 10⁻⁵ M in methanol and between 10⁻⁴ and 10⁻⁵ M in acetonitrile, as shown by increases in the molar conductivity values from those typical of 1:1 electrolytes to values representative of 2:1 electrolytes. In nitromethane there appears to be little dissociation at 10⁻⁵ M.

An aqueous solution of [Co(TIM)Cl₂]Cl rapidly changes color from the blue-green of [Co(TIM)Cl₂]⁺ to purple. The molar conductance of such a purple solution is 330 (10⁻³ M in cobalt), a value intermediate between that expected for a 2:1 and that for a 3:1 electrolyte.[15] Therefore the presence of a mixture of [Co(TIM)Cl(H₂O)]²⁺ and [Co(TIM)(H₂O)₂]³⁺ is suggested. The addition of HCl to a purple aqueous solution of [Co(TIM)Cl₂]Cl results in the return of the blue-green color characteristic of the [Co(TIM)Cl₂]⁺ ion.

Cobalt Complexes of DIM and DMC.—Condensation of N,N'-bis(3-aminopropyl)-1,2-diaminoethane (3.2.3) with biacetyl in methanol, followed by the addition of cobalt acetate, gives complexes of the ligand DIM (structure VII). The Co(II) derivatives can be isolated under an inert atmosphere whereas aerial oxidation of acid solutions gives the Co(III) compounds. The metathetical production of other derivatives and their interconversion reactions are entirely in accord with their formulation as *trans*-diacidocobalt(III) complexes. They all demonstrate 1:1 electrolyte behavior and analyze satisfactorily (analytical data are collected in Table I).[16]

In general, the infrared spectra of these complexes are almost identical with those of the nickel derivatives[17] and are strongly suggestive of the cyclic nature of the ligand, there being an absence of bands attributable to C=O and NH₂ groups but bands as-

(11) R. M. Pfeiffer, D. A. Baldwin, and N. J. Rose, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, No. INOR 47.

(12) L. Torre and E. C. Lingafelter have proven the structure of the ligand TIM by an X-ray structure determination on [Ni(TIM)(imadazole)₂]-(PF₆)₂: L. Torre, Thesis, University of Washington, 1971.

(13) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, 1955.

(14) J. Eliassaf, R. M. Fuoss, and J. E. Lind, Jr., *J. Phys. Chem.*, **67**, 1941 (1963).

(15) M. M. Jones, "Elementary Coordination Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1964, p 254.

(16) Unlike the reaction between diaminopropane and biacetyl to form TIM, DIM formation by condensation of 3.2.3 with biacetyl is particularly sensitive to excess acetate. Thus, in the presence of more than the quantity of cobalt acetate mentioned in the Experimental Section, a secondary product is formed which we believe may be the α-hydroxyamine monoimine macrocycle derived from DIM by the addition of water to one of its α-diimine–azomethine linkages. This reaction will be the subject of a later report.

(17) E. K. Barefield, Ph.D. Thesis, The Ohio State University, 1969.

signable as $\nu(C=N)$ modes appear at 1570–1590 and 1630–1640 cm^{-1}. A characteristic strong, sharp band at 1195 cm^{-1} compares with that at 1210 cm^{-1} in the TIM complexes. The N—H stretching modes of the secondary amine groups are generally seen as sharp single bands at 3210 cm^{-1}, except in the case of the dinitro complex, where the band is somewhat broader and shifted to lower frequency ($\sim$3145 cm^{-1}), possibly as a consequence of hydrogen bonding to the axial nitro groups.

The ligands TIM and DIM can be considered to be oxidized derivatives of 2,3,9,10-tetramethyl- and 2,3-dimethyl-substituted cyclam, the parent 14-membered macrocycle whose Co(III) complexes have been well characterized for some time.[4,5] The chemical reduction of these ligands (TIM and DIM) was therefore performed in order to verify in an unusual and unambiguous way the nature of the α-diimine-containing ligands. In addition, the successful preparation of complexes of the saturated ligands TMC and DMC would be an indication that numerous different kinds of cyclic secondary amines not available by any other method are accessible by the incorporation of suitable substituents into the amines or α-diketone components of the ligands TIM and DIM.

Reduction of the C=N groups in DIM and TIM complexes of cobalt has been achieved in methanol using hydrogen at 1 atm and activated Raney nickel (Catalyst-Grade 28, Davison Chemical Co.). Several features of the reduction reactions suggest, however, that they are substantially more complex than the hydrogenation of the corresponding nickel derivatives where the Raney nickel plays a normal catalytic role. The most significant of these are that the catalyst needs to be present in rather large quantities (at least 1 g/g of complex) and that reduction is accompanied by a series of color changes. Initially an air-sensitive red-purple solution of the cobalt(II) complex forms. This slowly turns deep blue, possibly indicating the presence of a Co(I) species, and finally a very pale, almost colorless solution results. Thus it appears that the activated Raney nickel serves both to reduce the metal ion and to assist in the hydrogenation process. The final solution is instantly air-oxidized to a brown solution, from which the product can be isolated readily.

By stopping the reaction at intervals, infrared spectra were used to show the appearance and subsequent reduction of long-lived intermediate species. The series of infrared spectra obtained during the course of the reduction of a sample of [Co(DIM)Br$_2$]ClO$_4$ is shown in Figure 2. The most striking, indeed almost the only, changes that occur during the early stages are the nearly total disappearance of the bands at 1560, 1200, and 930 cm^{-1} and concomitant appearance of the strong band at 1645 cm^{-1} (spectra a and b in Figure 2). This new band we assign to $\nu(C=N)$ of an isolated, nonconjugated azomethane linkage and this, together with the loss of the band at 1200 cm^{-1} assumed to be an α-diimine vibration, is evidence for the intermediate existence during the hydrogenation of a monoimine macrocycle.

On further hydrogenation, essentially the only infrared spectral change is the weakening and ultimate total disappearance of the 1645-cm^{-1} band (Figure
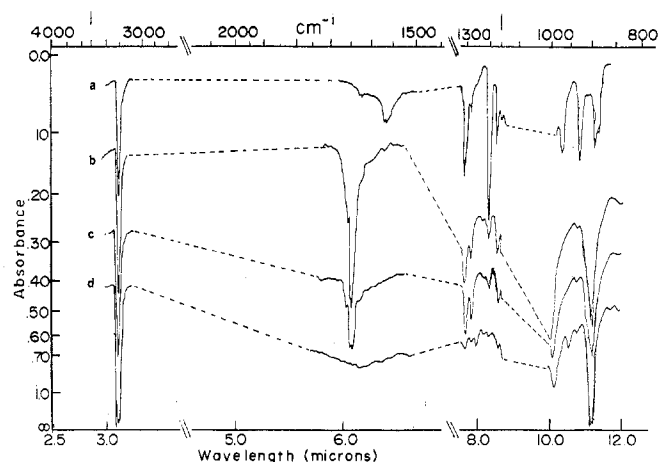

Figure 2.—Selected portions of the infrared spectra of [Co(DIM)Br$_2$]$^+$ and intermediates in the reduction of [Co(DIM)Br$_2$$^+$] to [Co(DMC)Br$_2$]$^+$: a, [Co(DIM)Br$_2$]ClO$_4$; b and c, intermediates; d, [Co(DMC)Br$_2$]ClO$_4$.

2, spectra c and d). The slightly broadened nature of the N–H stretching band in the spectrum of [Co(DMC)Br$_2$]ClO$_4$ produced in this way may be an indication that a mixture of stereoisomers is formed. Several isomeric forms of DMC are possible, some of which have been observed as nickel complexes,[17] but the separation and detailed characterization of these on cobalt(III) are outside the intended scope of this report. Complexes of the type [Co(DMC)X$_2$]Y were also synthesized from the free ligand using the methods by which Tobe, *et al.*, prepared the corresponding cyclam derivatives.[5] They were found to be identical in every way with those prepared by catalytic hydrogenation of DIM as detailed above. Metathetical production of other tetragonal complexes [Co(DMC)X$_2$]Y occurs normally; the representatives we prepared, their colors, and analytical data are shown in Table I. We have also made a cursory examination of the reduction at 1 atm hydrogen pressure of the complex [Co(TIM)Br$_2$]ClO$_4$, which is totally decomposed at higher pressures with this catalyst. Our results again show the presence of intermediates.

Nuclear Magnetic Resonance Spectra.—By analogy with the known structure of [Ni(TIM)(imidazole)$_2$]$^{2+}$ it can be inferred that the [Co(TIM)X$_2$]$^+$ species will have the five-membered chelate rings in a very nearly planar conformation and the six-membered chelate rings in a puckered conformation.[12] Two possible conformers thus result: one with both β-carbon atoms on the same side of the cobalt–imine plane and the other with one of the β-carbon atoms on one side of the plane and the second β-carbon atom on the other side of the plane. Since the interconversion of these two conformers involves only the rotation about carbon–carbon and carbon–nitrogen σ bonds and since there are no bulky constituents on the rings, rapid flexing between these two conformers is likely for the [Co(TIM)X$_2$]$^+$ ion in solution at or near room temperature. (See Figure 3 for labeling of the TMD ring.)

In principle, it is possible to detect rapid flexing (on the nmr time scale) by examination of the pmr spectrum of one of the [Co(TIM)X$_2$]$^+$ species. In a fixed conformation for the two TMD rings, the two

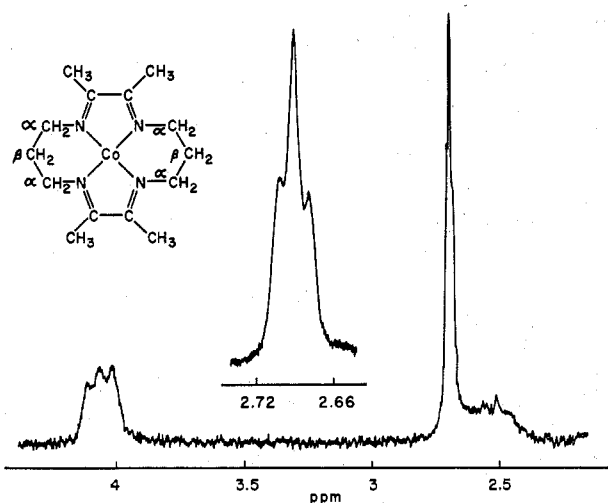Figure 3.—Pmr spectrum of [Co(TIM)Cl$_2$]PF$_6$ in CD$_3$CN at ambient temperature. The methyl resonance is shown at a smaller sweep width to reveal homoallylic coupling.

hydrogen atoms on the α carbons must be nonequivalent, one being axially disposed with respect to the cobalt–imine plane and one being equatorially disposed. Similarly, the hydrogen atoms on the β-carbon atoms must also be nonequivalent. Whereas, if rapid flexing is taking place, each hydrogen atom on the TMD backbone is flipping between an equatorial and an axial position so that the α-hydrogen atoms undergo environmental averaging, as do the β-hydrogen atoms. A very complex spectrum, an ABCDA'B' pattern, is predicted for the TMD protons in the fixed conformation case, but, if rapid flexing is occurring, a much simpler spectrum is expected in analogy to free TMD. The latter exhibits a downfield triplet arising from the α protons and an upfield quintet arising from the β protons, both multiplets being accounted for by first-order coupling between the α and β protons. As shown in Figure 3 the spectrum of [Co(TIM)Cl$_2$]$^+$ does show a broad triplet centered at 4.06 ppm ($J = 5$ Hz) and a second broad multiplet centered at 2.60 ppm. The triplet resonance is ascribed to the α protons whereas the broad upfield multiplet is assigned to the β protons. The observed patterns are certainly not characteristic of the complexity expected of an ABCDA'B' spectrum but neither are the observed patterns ascribed to the TMD ring the well-resolved triplet and quintuplet predicted by the simple flexing model offered above. In order to account more nearly for the nature of the observed spectrum the effects of coupling within this entire macrocyclic ring must be explored.

The methyl proton resonance appears as a sharp 1:2:1 triplet ($J = 1.2$ Hz) at 2.69 ppm. That the presence of a triplet is caused by coupling has been verified by double-resonance experiments to be described below and by the fact that the spacing of the triplet is invariant as observed on 60- or 100-MHz instruments. The coupling occurs between the methyl protons and the α protons of the TMD unit. It must be assumed that the TMD unit is undergoing rapid flexing on the nmr time scale, thus making the two α protons equivalent; otherwise the methyl proton resonance would not be expected to occur as a triplet. This coupling also accounts for the broad nature of the α-proton resonance which is split both by coupling

with the two β protons ($J = 5$ Hz) and with the three methyl protons ($J = 1.2$ Hz).

All of the peak assignments discussed above are strongly supported by several double-resonance experiments. In one experiment the triplet assigned to the α protons was irradiated giving rise to a singlet at 2.69 ppm instead of the triplet normally observed for this methyl proton resonance. Irradiation of the α-proton multiplet also produced a broad singlet at 2.60 ppm rather than the multiplet usually seen. In another experiment both the multiplet assigned to the β-proton peak and the methyl proton resonance were irradiated. A singlet resulted at 4.06 ppm.

In carbon compounds which have unsaturated linkages similar to the CH$_3$C=NCH$_2$ moiety found in complexes of TIM, splitting of the sort observed in the methyl proton resonance (Figure 3) has been attributed to long-range coupling through two single carbon–carbon bonds and one double carbon–carbon bond and has been named homoallylic coupling.[18] In the [Co(TIM)-Cl]$^+$ case, as well as in other complexes formed from biacetyl and TMD, the imine linkage is thought to act similarly to the carbon–carbon double bond in the homoallylic linkage. If the methyl protons do couple with the α protons by such a mechanism, the magnitude of the coupling constant should reflect the angle formed by the carbon–hydrogen bond of the α-carbon atom and the plane described by the imine linkage, the α-carbon atom, and the methyl carbon atom. This coupling is expected to be maximized when the angle is 90° and minimized when the angle is either 0 or 180° with the observed values ranging from 1 to 3 Hz.[18,19] If the TMD rings in the macrocycle are flexing rapidly, the coupling constant for the complex is expected to be the average of 0 and 3 Hz or $\sim$1.5 Hz, a value quite close to that actually observed. However, great care needs to be exercised in the interpretation of the magnitude of the homoallylic coupling constant because it is known to be solvent dependent in other compounds[18,20] and, in fact, is found to be solvent dependent in the [Co(TIM)Cl$_2$]$^+$ case also. Thus, the methyl proton resonance of the complex dissolved in acidic D$_2$O has nonresolvable side shoulders indicating a smaller J than the 1.2 Hz observed from the well-defined triplet shown in Figure 3. The effect has been observed in other complexes containing the grouping CH$_3$C=NCH$_2$–.[21]

Table II includes a summary of the observed pmr spectrum of [Co(DIM)Br$_2$]Br. The spectrum in neutral D$_2$O is broad and generally uninterpretable whereas if aqueous HBr is added to the sample, the spectrum becomes relatively sharp and some fine structure becomes apparent. In the spectrum obtained from the acidic solution there are two sharp peaks observed in the region expected for methyl protons and they are separated by only 1.5 Hz. Slightly upfield from the methyl resonances is a complex multiplet centered at 1.25 ppm. The relative area of this multiplet corresponds to that expected from the β protons of the TMD backbone, an assignment consistent with the relative chemical shift of this multiplet as com-

(18) S. Sternbell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

(19) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

(20) J. T. Pinkey and S. Sternbell, *Tetrahedron Lett.*, **4**, 275 (1963).

(21) L. G. Warner, N. J. Rose, and D. H. Busch, *J. Amer. Chem. Soc.*, **90**, 6938 (1968).

TABLE II
PMR DATA FOR COBALT COMPLEXES OF DIM AND DMC

Type of proton	Description of resonance	Chem shift, ppm	Rel area found (calcd)
	[Co(DIM)Br₂]Br[a]		
Methyl isomer A	Singlet	1.54 ⎫	
Methyl isomer B	Singlet	1.55 ⎭	6.0 (6)
β-TMD, both isomers	Complex multiplet	1.25	4.2 (4)
α-TMD and ethylene-diamine backbone, both isomers	Complex multiplet	1.80	12.0 (12)
	[Co(DMC)Br₂]PF₆[b]		
Methyl	Doublet (J = 6 Hz)	1.18	6.4 (6)
β-TMD	Complex multiplet	1.85	4.0 (4)
α-TMD and ethylene-diamine backbone and CH of reduced biacetyl backbone	Complex	2.65	15.0 (14)
NH	Broad doublet	5.2	. . . (4)

[a] Pmr spectrum of [Co(DIM)Br₂]Br in ~0.9 M DBr at ambient temperature. Chemical shifts are reported relative to the internal standard *tert*-butyl alcohol. Data taken from the 100-MHz spectrum. Samples prepared by first dissolving the complex in neutral D₂O and then adding 1 drop of concentrated aqueous HBr. [b] Pmr spectrum of [Co(DMC)Br₂]PF₆ in CD₃CN at ambient temperature. Chemical shifts are reported relative to internal TMS. Data taken from the 100-MHz spectrum.

acid is consistent with the postulate that one or more exchange processes have been quenched. Since rapid exchange of the amine protons is a requisite for rapid isomerization leading to loss of the two sharp methyl proton resonances, it is presumed that this change is the major one to be quenched.

By experiments and inferences similar to those just outlined the assignments were made in the case of [Co(DMC)Br₂]⁺ (see Table II). Comparison of the 60- and 100-MHz spectra of the same sample was again revealing. In contrast to the DIM case the doublet of the methyl resonance was found to arise from coupling (in this case with the proton originating from the reduction of the carbon atom of the C≕N moiety), a conclusion supported by a double-resonance experiment involving irradiation of the complex multiplet centered at 2.65 ppm. Upon irradiation the doublet at 1.18 ppm became a singlet. We conclude that, unlike the analogous DIM complex, only one of the stereoisomers exists in solution for [Co(DMC)Br₂]⁺.

Electronic Spectra.—In the discussion of the electronic spectra (Table III) we shall assume that all the complexes have tetragonal centric symmetry (D_{4h}). This requires that the macrocycles be coordinated in a planar fashion, assumptions which are especially justi-

TABLE III
VISIBLE–ULTRAVIOLET ABSORPTION SPECTRAL DATA
(BAND MAXIMA IN kK; MOLAR EXTINCTION COEFFICIENTS IN PARENTHESES)

Complex ion	Solvent	νE $^1E_g{}^a \leftarrow {}^1A_{1g}$	νA $^1A_{2g} \leftarrow {}^1A_{1g}$	νE+B $^1B_{2g} \leftarrow {}^1A_{1g}$ + $^1E_g{}^b \leftarrow {}^1A_{1g}$	Unassigned
[Co(TIM)Cl₂]⁺ [a]	Acetone	17.4 (46)	23.3 (144)[b]	25.2 (1100)	
[Co(TIM)Br₂]⁺ [a]	Acetone	16.9 (80)	Masked	25.5 (2680)	32.7 (~22,000)
[Co(TIM)I₂]⁺	Methanol	15.3 (<100)	20.85 (8800)	29.4 (18,800)	40.0 (~10,000), 45.5
[Co(TIM)(NO₂)₂]⁺	Water	23.40 (320)		27.8 (5600)	38.4
[Co(DIM)Cl₂]⁺	Methanol	16.4 (89)	Masked	25.2 (672)	
[Co(DIM)Br₂]⁺	Methanol	15.75 (99)	Masked	26.2 (2240)	32.9 (~25,000)
[Co(DIM)(NO₂)₂]⁺	Water	22.4 (233)		28.25 (9600)	39.1 (~37,000) 47.6 (~50,500)
[Co(DMC)Cl₂]⁺	Methanol	16.0 (112)	22.0 (112)	26.2 (185)	32.0 (~5000)
[Co(DMC)Br₂]⁺	Methanol	15.0 (41)	Masked	26.75 (2320)	
[Co(DMC)(NO₂)₂]⁺	Water	21.4 (435)		29.95 (6510)	39.4 (~41,000) 48.1 (~18,000)

[a] PF₆ salts used. [b] This is a shoulder on νE+B.

pared with the rest of the spectrum. A very complex multiplet with many peaks is centered at 1.80 ppm; it has a relative area corresponding to that expected from the sum of the α protons of the TMD backbone and the ethylenic protons. Confirmation of the peak assignments just outlined and some further interpretation of the assignments is made possible by comparison of the 60- and 100-MHz spectra obtained on the same sample. The separation between the two peaks assigned to the methyl proton resonance changes by a factor of 100:60, exactly the change expected if the two peaks were not related in any way by coupling. We conclude that both of the two major stereoisomers of [Co(DIM)Br₂]⁺ are present in solution, a contention in part supported by the fact that the ratio of the areas of the two peaks (1.55 and 1.54 ppm) to all others in the spectrum is the predicted value, 6:16 (see Table II). We have not attempted further analysis of the spectrum because of the extreme complexity caused by the overlapping nature of the patterns.

The sharpening of the spectrum upon addition of

fied for the ligand TIM[19] in view of the known structure of [Ni(TIM)(imidazole)₂]²⁺ and for DMC since Tobe, *et al.*,[5] have shown that cyclam (and hence DMC) has little tendency to form cis complexes with monodentate acido ligands under the conditions we have used.

Wentworth and Piper[22] have developed a crystal field model for the d–d transitions of a d⁶ ion in D_{4h} symmetry. The first band in an octahedral environment ($^1T_{1g} \leftarrow {}^1A_{1g}$) splits into two bands as the symmetry is reduced to D_{4h}, νE ($^1E_g{}^a \leftarrow {}^1A_{1g}$) and νA($^1A_{2g} \leftarrow {}^1A_{1g}$), respectively. This splitting is associated with a single tetragonal splitting parameter Dt. A positive Dt indicates that the in-plane ligand field is stronger than the axial field and *vice versa*. Application of this approach to these complexes leads to the ligand field splitting parameters Dq^{xy} associated with the planar ligands (*i.e.*, the macrocycle) and Dq^z relating to the axial groups. The equations which apply are

(22) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

$$\nu_A = 10Dq^{xy} - C \qquad (1)$$

$$Dt = (4/35)(10Dq^{xy} - \nu_E - C) \qquad (2)$$

$$Dq^z = Dq^{xy} - (7/4)Dt \qquad (3)$$

The interelectronic repulsion parameter C is taken to be 3800 K, a value shown by Wentworth and Piper[22] to be roughly independent of the field strength. Usually,[23] the arithmetic mean of the energies of the $^1A_{2g} \leftarrow {}^1A_{1g}$ transitions for a large number of complexes with the same planar ligands is used as ν_A in (1) so that an estimate of Dq^{xy} is available for use in (2) and (3) leading to values for Dt and Dq^z. Alternatively, a standard value for Dq^z can be used in eq 2 and 3 allowing access to Dq^{xy} and Dt values, and this approach has been used in the derivation of the quantities listed in Table IV.

TABLE IV
SPECTRAL PARAMETERS[a] FOR TETRAGONAL
DIHALOCOBALT(III) COMPLEXES

Complex	Dq^{xy}, K	Dt, K	Complex	Dq^{xy}, K	Dt, K
[Co(CR)Cl₂][+][b]	2830	785	[Co(cyclam)Cl₂][+][f]	2480	594
[Co(TIM)Cl₂][+]	2780	754	[Co(TIM)Br₂][+]	2860	903
[Co(1,7-CT)Cl₂][+]	2640	674	[Co(CR)Br₂][+][b]	2800	870
(isomer a)[c]			[Co(1,7-CT)Br₂][+][c]	2680	802
[Co(DIM)Cl₂][+]	2580	640	[Co(DIM)Br₂][+]	2630	775
[Co(β-CRH)Cl₂][+][d]	2580	640	[Co(β-CRH)Br₂][+][d]	2620	770
[Co(en)₂Cl₂][+][e]	2530	609	[Co(en)₂Br₂][+][e]	2530	714
[Co(DMC)Cl₂][+]	2500	595	[Co(DMC)Br₂][+]	2480	688

[a] $Dq^z(Cl^-) = 1460$ K and $Dq^z(Br^-) = 1277$ K have been used for these calculations. [b] Using data from K. M. Long, Ph.D. Thesis, The Ohio State University, 1967. [c] Reference 6. [d] Reference 7. [e] R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965). [f] Using data from ref 6.

In cases where both ν_E and ν_A are observed, the number of known values in eq 1–3 is greater than the number of unknown values (assuming that Dq^z and C are numbered among the known quantities). Thus, the internal consistency of the assignments can be estimated by comparing the value of ν_A as calculated from ν_E, Dq^z, and C with the observed value of ν_A. This has been done for [Co(TIM)Cl₂] and for [Co(DMC)Cl₂]⁺ where the calculated values are 24.0 and 21.2 kK, respectively. These values are in reasonable agreement with the observed ν_A's, 23.3 and 22.0 kK (Table III), a fact suggesting that the Wentworth–Piper approach is acceptable for the complexes considered here. The appropriateness of the Wentworth–Piper approach is further indicated in that the values of Dq^{xy} calculated from the spectral data for the bis chloro and bromo complexes containing the same in-plane ligand are nearly the same (see eq 1 and Table III). Consequently, we feel justified in entering into a discussion of the trends revealed in the Table IV while admitting that the exact magnitudes of the calculated parameters would probably not be the same as those derived through these approximate approaches. Thus, it must be noted that the foregoing method of calculation has been criticized by Rowley and Drago[24] since this method does not account for configuration interaction; however, more complete treatments require more data than the spectra of these complexes provide.

The overall pattern revealed by Table IV for these 14-membered tetradentate macrocyclic ligands is as

expected (see introductory material). The strength of the ligands (*i.e.*, Dq^{xy}) increases steadily, for both the bis chloro and bromo complexes, as the extent of unsaturation in the ligand increases. Further, the value of Dq^{xy} for DMC obtained from our spectral data compares well with that for cyclam obtained from published spectral data.[6] It is particularly interesting to note that these two saturated cyclic ligands exert a field on Co(III) similar to or perhaps even slightly smaller than that exerted by ethylenediamine, as was mentioned earlier.[23] This behavior is in marked contrast to the case of Ni(II), where two of the relevant quantities are Dq^{xy}(cyclam) = 1460 K[25] and Dq^{xy}((en)₂) = 1150 K.[25] A somewhat unexpected result is that the pyridine nitrogen atom, the two adjacent imine nitrogen atoms, and the secondary amine of CR (structure IV) provide essentially the same field as do the two α-diimine moieties of TIM. The pattern continues in that the reduction of the two imines in CR and the effective loss of one α-diimine unit in TIM give rise to two ligands, CRH and DIM, for which the Dq^{xy} values are indistinguishable. The relative effect on the in-plane field of a pyridine nitrogen atom can also be estimated by comparing the Dq^{xy} values for β-CRH and for 1,7-CT (see Table IV). Thus a combination of one pyridine nitrogen atom and one amine nitrogen atom contributes almost as much to the field as do two azomethine linkages. The values of Dt are markedly greater for the stronger macrocyclic ligands within each series as expected and those for the chloro complexes range from 85 to 149 K less than those for the corresponding bromo complexes.

If an average value of 2820 K is assumed for Dq^{xy} of [Co(TIM)X₂]⁺, then we calculate $Dt = 1040$ K and $Dq^z = 1000$ K for the iodide ligand. This compares favorably with the values for Dq^z of iodide: [Co(CRH)ICl]⁺, 1020 K;[7] [Co(CR)I₂]⁺, 900 K;[26] [Co(NH₃)₅I]²⁺, 970 K.[22] Rather few diiodocobalt(III) complexes have been reported, the more well-known ones being [Co(diars)₂I₂]⁺,[27] [Co(CR)I₂]⁺,[26] and those including dimethylglyoxime and its mononegative anion as ligands in the plane.[28] Consequently, the spectrum of [Co(TIM)I₂]I deserves further mention. The features are very similar to those for [Co(CR)I₂]⁺ in the only other reported spectrum. Their most striking characteristic is the very high intensity of the band tentatively assigned to the ν_A transition: ϵ_A(TIM) = 9000 and ϵ_A(CR) = 10,000. These high intensities may be due, in part, to the reducing nature of the iodide ion,[29] and/or they may arise from "intensity stealing" from the even more intense third bands nearby: ϵ(TIM) = 19,000 and ϵ(CR) = 18,000. In this context we note that the molar extinction coefficients of the ν_A bands in complexes of the [Co(L)(iodide)X]⁺ type (where L = in-plane ligand or ligands and X = other axial ligand) are always much higher than for those species of the [Co(L)X₂]⁺ type, usually being 1000 or more (see for example spectra of [Co(*meso*-CRH)ICl]⁺, [Co(CR)I(H₂O)]²⁺,[26] and [Co(NH₃)₅-

(23) For example see D. H. Busch, *Helv. Chim. Acta*, Fasciculus Extraordinarius, Alfred Werner, 174 (1967).

(24) D. A. Rowley and R. S. Drago, *Inorg. Chem.*, **7**, 795 (1968).

(25) C. R. Sperati, Thesis, The Ohio State University, 1971; A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, New York, N. Y., 1968.

(26) K. M. Long, Ph.D. Thesis, The Ohio State University, 1967.

(27) R. S. Nyholm, *J. Chem. Soc.*, 2071 (1950).

(28) A. V. Ablov, *Bull. Soc. Chim. Fr., Mem.*, [5] **7**, 151 (1940).

(29) C. J. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Elmsford, N. Y., 1962, p 140.

I]$^{2+}$ [22]). Thus the iodide ligand in complexes of this type most likely falls into its usual place in the hyperchromic series of Jørgensen.[29]

Polarographic Data.—It is well known[30] that studies of the electrochemical behavior of metal complexes shed considerable light on the interactions between the metal and the ligands. This principle has prompted interest recently[31] in the polarographic behavior of complexes of macrocyclic ligands because they allow control of such variables as the nature of the ligand fields and also because we anticipate that some of these ligands are capable of stabilizing unusual metal oxidation states. The results of a complete study of the electrochemistry of the systems described in this report will be described later.[32] The polarographic data for the nitro complexes are contained in Table V. The cyclam

TABLE V
HALF-WAVE POTENTIALS FROM VOLTAMMETRY
OF THE COMPLEXES[a,b]

Complex	$E^1_{1/2}$, V	$E^2_{1/2}$, V
[Co(cyclam)(NO$_2$)$_2$]$^+$	−0.450	
[Co(DMC)(NO$_2$)$_2$]$^+$	−0.450	
[Co(DIM)(NO$_2$)$_2$]$^+$	−0.266	−0.841
[Co(TIM)(NO$_2$)$_2$]$^+$	−0.217	−0.474

[a] [Complex] = saturated solutions of the ClO$_4^-$ salts in 5 × 10^{-2} M Et$_4$NClO$_4$, methanol solution. [b] See reference electrode; rotating platinum electrode.

derivative is included merely to illustrate the negligible effect of methyl substituents on DMC. The nitro complexes have been chosen in order that the possibility of loss of the axial ligands in the solutions be minimized.

The data show that the first half-wave potential becomes more anodic (*i.e.*, the reduction Co(III) → Co(II) becomes easier) as the degree of unsaturation of the ligand increases, as has been observed for other macrocycles.[31c] This suggests that the greater nephalauxetic effect associated with the unsaturated ligands allows more extensive delocalization of the d electrons and hence facilitates the reduction process. Thus we expect, and observe, the first half-wave potential for [Co(TIM)(NO$_2$)$_2$]$^+$ to be more positive than that for [Co(DIM)(NO$_2$)$_2$]$^+$. In addition, there will be less repulsion of the second electron to be added, so the Co(II) → Co(I) reduction should also be substantially easier for TIM complexes than for DIM complexes, as is shown by the relative positions of the second cathodic waves. In other words, the data illustrate clearly that there is greater M–L π bonding for the more highly unsaturated ligands, implying that metal ions in low valence states should be considerably stabilized with respect to oxidation when encompassed by a "soft" macrocycle such as TIM.

Experimental Section

The reagents used as starting materials were obtained commercially and used without further purification. All solvents were of reagent grade quality. The products were dried at room temperature for 12 hr at ~1 mm pressure.

(30) A. A. Vleck, *Progr. Inorg. Chem.*, **5**, 211 (1967).

(31) For example: (a) D. C. Olson and J. Vasilevskis, *Inorg. Chem.*, **8**, 1611 (1969); (b) J. M. Palmer, E. Papaconstantinou, and J. Endicott, *ibid.*, **8**, 1516 (1969); (c) K. Farmery, V. Katovic, N. E. Tokel, D. H. Busch, and L. B. Anderson, *J. Amer. Chem. Soc.*, **92**, 400 (1970); (d) E. K. Barefield, F. V. Lovecchio, N. E. Tokel, and E. Ochiai, *Inorg. Chem.*, **11**, 283 (1972).

(32) N. E. Tokel, F. V. Lovecchio, and D. H. Busch, to be submitted for publication.

1,3-Diaminopropane-2-(Hydrogen chloride) (TMD·2HCl).—TMD (100 ml) was dissolved in 200 ml of 95% ethanol and cooled to 2° in an ice bath. Concentrated HCl (328 ml) was added slowly at such a rate that the temperature was kept below 10°. The white crystalline product, TMD·2HCl, was collected, washed with anhydrous ether, and dried.

Synthesis of the *trans*-Diacido-2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraenecobalt(III) Complexes, [Co(TIM)X$_2$]Y. *trans*-[Co(TIM)Cl$_2$]PF$_6$.—The following procedure was carried out with no attempt made to protect the reaction mixture from the atmosphere. A slurry of TMD·2HCl (5.88 g, 40 mmol) in 15 ml of absolute methanol was cooled at <2° in an ice bath and then biacetyl (3.45 g, 40 mmol) in 10 ml of methanol was added. With constant stirring, a solution of KOH (2.24 g, 40 mmol) in 35 ml of methanol was added dropwise while keeping the temperature below 5°. This milky yellow reaction mixture was stirred for 15 min at 2° and then a solution of Co(OAc)$_2$·4H$_2$O (5.00 g, 20 mmol) in 150 ml of methanol was added. The resulting mixture was allowed to warm to room temperature and was stirred for an additional 12 hr. A solution of NaPF$_6$ (3.36 g, 20 mmol) in 20 ml of methanol was added to the filtered reaction mixture resulting in the precipitation of blue-green crystals of [Co(TIM)Cl$_2$]PF$_6$; yield 3.5 g (30%). The product was recrystallized from a hot (55°) acetone–water mixture (50:50 by volume), containing concentrated aqueous HCl by cooling in an ice bath. Typical amounts for this recrystallization are 0.5 g of [Co(TIM)Cl$_2$]FP$_6$, 15 ml of acetone–water, and 1 ml of concentrated HCl.

trans-[Co(TIM)Cl$_2$]Cl.—A saturated solution of LiCl in acetone was added slowly to a saturated solution of [Co(TIM)Cl$_2$]PF$_6$ in acetone until the solution became cloudy. Upon cooling, light green crystals appeared; yield 95%.

trans-[Co(TIM)Br$_2$]PF$_6$.—Concentrated HBr (1 ml of 9 M solution) was added to a boiling solution of [Co(TIM)Cl$_2$]PF$_6$ (0.5 g) in 100 ml of acetone–water mixture (50:50 by volume). The solution was boiled for 5 min and then set aside to cool. Upon cooling to room temperature, the solution deposited dark green crystals of [Co(TIM)Br$_2$]PF$_6$; yield 85%.

trans-[Co(TIM)Br$_2$]Br. **Procedure A.**—[Co(TIM)Br$_2$]Br was prepared from [Co(TIM)Br$_2$]PF$_6$ by the same procedure that was used to prepare [Co(TIM)Cl$_2$]Cl from [Co(TIM)Cl$_2$]PF$_6$.

Procedure B.—Hydrobromic acid (32.6 g of 48% aqueous solution; 0.2 M) was added slowly to a solution of 1,3-diaminopropane (15 g, 0.2 M) in methanol (600 ml). Biacetyl (17.2 g, 0.2 M) was then added and the mixture was stirred. After 30 min, cobalt(II) acetate, Co(OAc)$_2$·4H$_2$O (24.9 g, 0.1 M), was added and the mixture was stirred under nitrogen for 3 hr. To the resulting deep purple solution, hydrobromic acid (*ca*. 70 ml) was added, and then air was bubbled through the mixture until precipitation of the product was complete. The resulting lime green solid was washed with methanol containing hydrobromic acid and then recrystallized from hot 5% aqueous hydrobromic acid. The final product, deep green plates, was washed with a small amount of methanol and then ether and dried; yield ~30%.

trans-[Co(TIM)Br$_2$]ClO$_4$.—Addition of a saturated solution of sodium perchlorate, or of 70% aqueous perchloric acid, to an aqueous or methanolic solution of [Co(TIM)Br$_2$]Br gave green crystals of the product in essentially quantitative yield.

trans-[Co(TIM)Cl$_2$]ClO$_4$.—Use of the corresponding quantity of hydrochloric acid in a procedure similar to that described above for the preparation of [Co(TIM)Br$_2$]Br (procedure B) gave no solid product. Addition of perchloric acid to the final reaction solution caused precipitation of a gray-green powder. This was filtered, washed with methanol, and then recrystallized from acetonitrile containing hydrochloric acid.

trans-[Co(TIM)I$_2$]I.—Use of hydriodic acid instead of hydrobromic in a procedure identical with that leading to [Co(TIM)Br$_2$]Br (procedure B) gave green-brown crystals of [Co(TIM)I$_2$]I. The product was filtered, washed with methanol, and recrystallized from hot water containing a little hydroiodic acid. The large, thin plates of product (yield ~15%) appear green by reflected light and yellow by transmitted light.

trans-[Co(TIM)(NO$_2$)$_2$]ClO$_4$.—On the addition of an aqueous solution of sodium nitrite to a solution of [Co(TIM)Br$_2$]Br, there was an immediate color change from green to yellow-orange. Addition of perchlorate caused crystallization of the product; yield ~85%.

Synthesis of the *trans*-Diacido-2,3-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,3-dienecobalt(III) Complexes, [Co(DIM)X$_2$].

trans-[Co(DIM)Br₂]ClO₄.—Hydrobromic acid (3.26 g of 48% aqueous solution, 0.02 M) was added to a solution of N,N'-bis(3-aminopropyl)-1,2-diaminoethane (3.48 g, 0.02 M), followed by biacetyl (1.72 g, 0.02 M). After the solution had been stirred for 0.5 hr, resulting in a yellow-brown color, cobalt(II) acetate (2.49 g, 0.01 M) was added and the mixture was stirred under nitrogen for 4 hr. Excess hydrobromic acid was added to the purple solution, which turned green when air was bubbled through it. Addition of perchloric acid caused crystallization of the product as a bright green solid which was filtered, washed with methanol, and dried by vacuum desiccation.

trans-[Co(DIM)Br₂]PF₆.—Addition of a saturated acetonitrile solution of [Co(DIM)Br₂]ClO₄ to a saturated aqueous solution of NH₄PF₆ caused precipitation of the PF₆ salt.

trans-[Co(DIM)Br₂]Br.—Solid [Co(DIM)Br₂]ClO₄ was stirred in a saturated acetone solution of LiBr. Over a period of 1 hr the solid [Co(DIM)Br₂]ClO₄ disappeared and [Co(DIM)Br₂]Br precipitated.

trans-[Co(DIM)Cl₂]ClO₄ or -PF₆.—Use of hydrochloric acid instead of hydrobromic acid in the procedure described above for the preparation of [Co(DIM)Br₂]ClO₄ leads to the corresponding *trans*-dichloro complex.

trans-[Co(DIM)(NO₂)₂]ClO₄.—This was prepared by the addition of sodium nitrite to the bromo or chloro complex, in a manner identical with that described for the synthesis of the corresponding TIM complex.

Synthesis of 2,3-Dimethyl-1,4,8,11-tetraazacyclotetradecane (DMC).—Hydrogenation of [Ni(DIM)](ClO₄)₂ in methanol using active Raney nickel as catalyst gave [Ni(DMC)](ClO₄)₂ in good yield.[17] The free cyclic amine was then removed from nickel following the method of Curtis.[33] Decomposition of [Ni(DMC)](ClO₄)₂ was achieved with 5 equiv of sodium cyanide in a 1:1 ethanol–water solution. The ethanol was removed by rotary evaporation and the product was extracted into chloroform. Removal of the chloroform gave the crude product as an off-white solid, which was recrystallized from dioxane. This was analyzed as the hydrochloride salt. *Anal.* Calcd for C₁₂H₃₂N₄Cl₄: C, 38.5; H, 8.6; N, 15.0; Cl, 38. Found: C, 36.9; H, 8.3; N, 14.3; Cl, 36.2.

Complexes of DMC.—These complexes may be prepared from

free ligand following the procedures used by Bosnich, Poon, and Tobe.[34] Alternatively, the cobalt complexes of DIM can be reduced directly. The case of [Co(DMC)Br₂]ClO₄ is given here as an example. Green [Co(DIM)Br₂]⁺ changed to a red-yellow color in CH₃OH solution upon the addition of Raney nickel hydrogenation catalyst. The necessary 2 mol of hydrogen was absorbed in about 2 min at 50 lb H₂ pressure. The pale yellow solution was filtered in the presence of air and HBr was added. The resulting green solution was evaporated to a small volume and saturated with NaClO₄. Yellow-green [Co(DMC)Br₂]ClO₄ separated from solution. Recrystallization yielded yellow-green crystals.

Physical Measurements.—Using KBr plates infrared spectra were obtained with a Beckman IR-10 recording spectrophotometer and Perkin-Elmer Model 337 spectrophotometer as Nujol and halo oil mulls in the range 4000–400 cm⁻¹. A Cary Model 14R spectrophotometer was used for visible spectra in the range 12.5–33.0 kK. The electronic spectra of [Co(TIM)Cl₂]⁺ and [Co(TIM)Br₂]⁺ were resolved using a Du Pont 310 curve resolver programmed for gaussian distribution. Solution conductivities were obtained with an Industrial Instruments, Inc., Model RC-16B2 conductivity bridge at 25 ± 0.1°.

Pmr spectra were run on a Varian HA-60/DA-60 and a Varian HA-100 spectrometer at ambient temperature. Elemental analyses were determined by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach über Engelskirchen, West Germany, Galbraith Laboratories, Inc., and Chemalytics, Inc.

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Monoalkyl Derivatives of the Cobalt(III) Complexes of a Tetradentate Macrocyclic Ligand Containing α-Diimine Groups

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The tetradentate macrocycle 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene (abbreviated Me₄[14]-1,3,8,10-teteneN₄ or more simply Me₄[14]teteneN₄), in which two conjugated α-diimine functional groups are coordinated about the metal in a planar array, has been used to produce cobalt(III) complexes containing a σ-bound alkyl group (R) as one of the axial ligands. These complexes have been prepared by standard methods *via* the corresponding cobalt(I) derivatives Coᴵ(Me₄[14]teteneN₄)X (X = halide). Direct reaction between the cobalt(II) derivatives [Co(Me₄[14]teteneN₄)X]⁺ and alkyl halides results in formation, in ~50% yield, of the same alkylcobalt(III) complexes—a reaction which is rationalized in terms of the free-radical-like nature of the d⁷ metal ion. These complexes have been identified as six-coordinate alkylcobalt(III) complexes by use of analytical, electrical conductivity, and spectral (nmr, infrared, and electronic) data.

Introduction

As part of an extensive investigation of the use of synthetic macrocyclic ligands in providing chemical foundations for the understanding of the behavior of natural macrocyclic complexes,[1] we have been examining the ligand structural parameters that are respon-

sible for the successful synthesis of compounds containing Co(III)–C bonds.[2] Among the factors that might be important in this respect are the nature of the donor atoms, the sizes of chelate rings, the charge on the macrocyclic ligand, and the nature and extent of delocalization of any unsaturation in the system. There are now several noncyclic polydentate ligand

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