salicylaldimines, the R = $C_6H_5CHCH_3$ compound is 15% tetrahedral while the R = *sec*-C_4H_9 and *i*-C_3H_7 compounds are about 50% tetrahedral under the same experimental conditions.[2,3] It can be concluded that the nonaromatic dimedone ring promotes a planar configuration of bidentate Schiff base complexes of nickel(II) to a significantly greater extent than does either the open chain of the β-ketoamines or the aromatic ring of the salicylaldimines. Also the dimedone ring inhibits intermolecular association to a greater degree than do the other two ligand "backbones."

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CONTRIBUTION FROM THE MCPHERSON AND EVANS CHEMICAL LABORATORIES,
THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO 43210

Stereospecific Formation of Chelate Sandwich Compounds Derived from *o*-Aminobenzaldehyde and 2-Amino-5-chlorobenzaldehyde by a Metal Ion Induced Rearrangement

BY LARRY T. TAYLOR[1] AND DARYLE H. BUSCH

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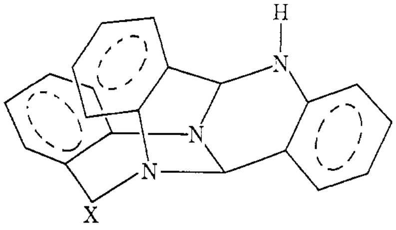
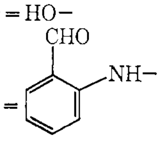
13-Hydroxy-6,12-benzo-6H-quinazolino[3,4-*a*]quinazoline $(oab)_3$ rearranges under the influence of nickel(II) ion to produce the known closed tridentate macrocyclic ligand tribenzo[*b*,*f*,*j*][1,5,9]triazacycloduodecine (TRI). This metal ion induced rearrangement has been used to synthesize a complex containing two trimeric condensates bound to each nickel(II) ion, $Ni(TRI)_2^{2+}$. The resultant complexes exhibit octahedral stereochemistry with the three donor nitrogen atoms of each macrocycle occupying a face of the octahedron. Two geometrical arrangements are possible for these complexes depending upon the clockwise or counterclockwise progression of the repeating unit (as viewed down the major threefold axis of rotation) in each macrocyclic Schiff base moiety. Reactions with partially resolved $Ni(TRI)(H_2O)_3^{2+}$ indicate that $Ni(TRI)_2^{2+}$ exists in the *meso* form exclusively.

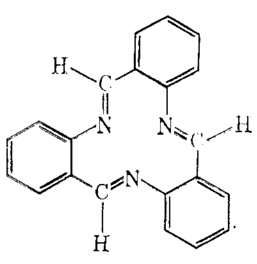
Introduction

The metal ion controlled stereochemical course of a chemical reaction is dramatically demonstrated in the self-condensation of *o*-aminobenzaldehyde. A bis anhydro trimer, $(oab)_3$ (Ia), and tris anhydro tetramer (Ib) are produced in the absence of metal ions;[2] whereas in the presence of nickel(II) ion, two complexes containing closed tridentate[3] (TRI) and tetradentate[4] (TAAB) macrocyclic ligands, respectively, are isolated. The tridentate ligand is shown as II. A complex possessing solely the tetradentate macrocyclic ligand is prepared in the presence of copper(II).[4] The structures of the ligands in these complexes have been established by X-ray studies.[5]



Ia, X— = HO—

Ib, X— =




II

In a previous communication we reported preliminary results[6] concerning the role of the metal ion in these self-condensation reactions in addition to the preparation of a novel chelate sandwich compound. We wish now to report these findings in more detail as well as to describe a unique stereospecific reaction involving these materials.

Experimental Section

Materials.—*o*-Aminobenzaldehyde and 2-amino-5-chlorobenzaldehyde were prepared by the method of Smith and Opic[7] using 2-nitrobenzaldehyde and 5-chloro-2-nitrobenzaldehyde as precursors. The method described by McGeachin[2] was employed

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[1] National Institutes of Health postdoctoral fellow, 5-F2-GM-28, 091-03.

[2] S. G. McGeachin, *Can. J. Chem.*, **44**, 2323 (1966).

[3] G. A. Melson and D. H. Busch, *J. Am. Chem. Soc.*, **87**, 1706 (1965).

[4] G. A. Melson and D. H. Busch, *ibid.*, **86**, 4834 (1964).

[5] E. B. Fleischer and E. Klem, *Inorg. Chem.*, **4**, 637 (1965); S. W. Hawkinson and E. B. Fleischer, private communication, 1968.

[6] L. T. Taylor, S. C. Vergez, and D. H. Busch, *J. Am. Chem. Soc.*, **88**, 3170 (1966).

[7] L. I. Smith and J. W. Opie, *Org. Syn.*, **28**, 11 (1948).

TABLE I
ANALYTICAL DATA FOR THE NICKEL(II) COMPLEXES

	Calcd, %						Found, %					
	C	H	N	Halogen	S	P	C	H	N	Halogen	S	P
$Ni(TRI)_2(NO_3)_2 \cdot H_2O$	61.56	3.94	13.68	...	...	..	61.63	3.28	13.45	...	...	...
$Ni(TRI)_2(PF_6)_2$	52.14	3.13	8.67	23.57	...	6.40	51.95	3.28	8.59	22.89	...	6.21
$Ni(TRI)_2(SCN)_2$	65.11	3.97	13.81	...	7.90	...	65.47	4.03	13.95	...	7.93	...
$Ni(TRI)_2Cl_2 \cdot H_2O$	65.82	4.21	10.97	9.25	...	...	65.61	4.47	11.26	9.13	...	...
$Ni(TRI)_2Br_2 \cdot H_2O$	58.98	3.77	9.83	18.69	...	...	59.23	3.89	9.81	18.86	...	...
$Ni(TRI)_2I_2 \cdot H_2O$	53.14	3.40	8.85	26.74	...	...	53.07	3.86	8.62	26.51	...	...
$Ni(TRI)_2(ClO_4)_2$	57.56	3.45	9.59	8.09	...	...	56.96	3.70	9.27	8.03	...	...
$Ni(5\text{-}Cl\text{-}TRI)(NO_3)_2 \cdot C_2H_5OH$	43.06	2.81	10.92	16.58	...	...	42.83	3.01	10.43	16.58	...	...
							43.19	1.90	11.20	16.13		
							42.74	2.86	10.55	16.59		
							42.64	2.76	10.84	16.34		
$Ni(5\text{-}Cl\text{-}TRI)(NO_3)_2 \cdot H_2O$	41.11	2.30	11.42	17.34	...	...	41.48	2.45	11.39	16.96	...	...
$Ni(5\text{-}Cl\text{-}TRI)(TRI)(NO_3)_2 \cdot 2H_2O$	53.61	3.32	11.91	11.30	...	...	53.1	3.23	11.60	11.55	...	...
							53.0	3.08	11.45			
								3.35	12.04			

for the preparation of 13-hydroxy-6,12-benzo-6H-quinazolino-[3,4-*a*]quinazoline $(oab)_3$. The acid-catalyzed self-condensation product of 2-amino-5-chlorobenzaldehyde was prepared by dissolving approximately 8 g of the above in 1500 ml of distilled water maintained at 50° under nitrogen. After complete dissolution, 12 ml of concentrated HCl in 100 ml of water was added to the saturated solution. Although within 5 min a pale yellow compound began to precipitate, the solution was allowed to stand for 1 day. The pale yellow material was then filtered, washed with a 2% aqueous solution of $NaHCO_3$, and dried at room temperature under reduced pressure for 12 hr. The crude material was used in all reactions. All other chemicals were obtained commercially and were of reagent grade or equivalent.

Preparation of Bis(tribenzo[*b,f,j,*][1,5,9]triazacycloduodecine)nickel(II) Nitrate Monhydrate.—A solution of 1.16 g (0.004 mol) of nickel(II) nitrate hexahydrate dissolved in 30 ml of methanol was added to a warm suspension of 2.60 g (0.008 mol) of 13-hydroxy-6,12-benzo-6H-quinazolino[3,4-*a*]quinazoline in 30 ml of anhydrous methanol. Upon reflux for 2 hr, the bis anhydro trimer $(oab)_3$ dissolved initially giving an orange-yellow solution which slowly turned wine red. After cooling to room temperature, red-brown crystals deposited on the walls of the reaction vessel. The red-brown material was collected and recrystallized from warm methanol, filtered, and dried *in vacuo* over P_2O_5 at room temperature, yielding 2.5 g of $Ni(TRI)_2(NO_3)_2 \cdot H_2O$.

The same material was prepared by adding 1.02 g (0.002 mol) of $Ni(TRI)(NO_3)_2 \cdot H_2O$ dissolved in 50 ml of methanol to a suspension of 0.65 g (0.002 mol) of the bis anhydro trimer $(oab)_3$ in 20 ml of methanol and refluxing for 10 hr. The product was isolated in the manner described above.

Preparation of Other Derivatives of Bis(tribenzo[*b,f,j*][1,5,9]-triazacycloduodecine)nickel(II).—To a saturated solution of the nitrate salt in methanol at room temperature was added an excess of either the lithium, the sodium, or the ammonium salt of the required anion, dissolved in a minimum amount of methanol. In the cases of thiocyanate, perchlorate, iodide, and hexafluorophosphate, the desired salts precipitated immediately. The bromide and chloride salts crystallized on standing overnight in a refrigerator. All products, except the PF_6^- derivative, were recrystallized from warm methanol and dried *in vacuo* at room temperature over P_2O_5. The PF_6^- salt was recrystallized from hot reagent acetone. Analytical data for these compounds are reported in Table I.

Preparation of Derivatives of Tri-5-chlorobenzo[*b,f,j*][1,5,9]-triazacycloduodecinenickel(II).—To a solution prepared by dissolving 1.30 g (0.003 mol) of crude 5-chloro-2-aminobenzaldehyde in 20 ml of absolute ethanol was added 0.87 g (0.003 mol) of $Ni(NO_3)_2 \cdot 6H_2O$. The resulting mixture was refluxed for 4 hr during which time an orange-yellow crystalline product appeared in the reaction vessel. This material was filtered, washed with ethanol, and dried for 12 hr at reduced pressure over P_4O_{10}. The material which was isolated was found to have the composition $Ni(5\text{-}Cl\text{-}TRI)(NO_3)_2 \cdot C_2H_5OH$. This material could be recrystallized from warm methanol to yield another product of the composition $Ni(5\text{-}Cl\text{-}TRI)(NO_3)_2 \cdot H_2O$. See Table I for analytical data.

Preparation of Tri-5-chlorobenzo[*b,f,j*][1,5,9]triazacycloduodecinetribenzo[*b,f,j*][1,5,9]triazacycloduodecinenickel(II) Nitrate Dihydrate.—To a solution prepared by dissolving 0.64 g (0.001 mol) of $Ni(5\text{-}Cl\text{-}TRI)(NO_3)_2 \cdot C_2H_5OH$ in 100 ml of a warm 70% by volume methanol–ethylene glycol mixture was added 0.33 g (0.001 mol) of the solid bis anhydro trimer derived from *o*-aminobenzaldehyde. The resulting mixture was refluxed overnight and then cooled, whereupon a red-brown material crystallized. The material was recrystallized from hot methanol and dried *in vacuo* for 12 hr over P_4O_{10}. The material had the composition $Ni(5\text{-}Cl\text{-}TRI)(TRI)(NO_3)_2 \cdot 2H_2O$. See Table I.

Physical Measurements.—Infrared spectra were determined by the potassium bromide pellet and Nujol mull techniques with a Perkin-Elmer Model 337 recording spectrophotometer. Electronic absorption spectra were obtained in solution with a Cary Model 14 recording spectrophotometer. Diffuse transmittance spectra were obtained using Nujol mulls supported on filter paper.[8]

Molar conductances were measured using an Industrial Instruments Inc. Model RC-16B conductivity bridge and a cell with a constant of 2.116 cm^{-1}. The reagent grade methanol used for these measurements had a specific conductance of less than 10^{-6} ohm^{-1}.

Magnetic susceptibility data were obtained at room temperature by either the Gouy or Faraday method using mercury(II) tetrathiocyanatocobaltate(II) as the calibrant. The susceptibilities of ligands and anions were calculated from Pascal's constants.[9]

Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and in this laboratory.

Results and Discussion

13-Hydroxy-6,12-benzo-6H-quinazolino[3,4-*a*]quinazoline, $(oab)_3$, rearranges under the influence of nickel(II) ion to give the cationic complex of the tridentate ligand (II). The rearrangement can be accomplished by heating equimolar quantities of $(oab)_3$ and $Ni(NO_3)_2 \cdot 6H_2O$ or $NiCl_2 \cdot 6H_2O$ in either ethanol, methanol, acetonitrile, 1-butanol, or ethylene glycol. No tetrameric condensate is formed in contrast to the result when *o*-aminobenzaldehyde undergoes self-condensation in

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(8) R. H. Lee, E. Griswold, and J. Kleinberg, *Inorg. Chem.*, **3**, 1278 (1964).

(9) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960.

the presence of nickel(II) ion. The rearrangement product has the same composition and chemical and physical properties as reported earlier.[3]

The tris anhydro tetramer (oab)$_4$ (Ib) also rearranges under similar conditions in the presence of nickel(II) ion, but a mixture of trimeric and tetrameric condensates is produced.[4] The copper(II)-induced rearrangement of both (oab)$_3$ and (oab)$_4$ produces solely the cationic complex of the tetrameric Schiff base ligand.

Apparently an extreme labilization of the organic substrate accompanies the rearrangement process before termination in a stable product, as dictated by the most thermodynamically stable coordination polyhedron of the metal ion. Metal ions favoring octahedral coordination (Ni(II)) may form stable products in which are bound either three mutually *cis* positions (trimeric condensate) or four mutually planar positions (tetrameric condensate). On the other hand, metal ions that bind donor atoms more firmly in a fourfold planar array (Cu(II)) should strongly favor the cyclic tetramer.

In conjunction with this investigation, crude 2-amino-5-chlorobenzaldehyde and its bis anhydro trimer were prepared. Comparison of the infrared spectra of the chloro- and unsubstituted derivatives support this conclusion. These are new organic compounds. Refluxing 2-amino-5-chlorobenzaldehyde and $Ni(NO_3)_2 \cdot 6H_2O$ in ethanol or methanol for 24 hr gave no evidence for the formation of a nickel-containing product. The color of the solution did not change from its original pale green hue. In contrast, an ethanol solution of crude bis anhydro trimer of 2-amino-5-chlorobenzaldehyde was found to rearrange in the presence of $Ni(NO_3)_2 \cdot 6H_2O$ to yield the bright orange $Ni(5\text{-}Cl\text{-}TRI)(NO_3)_2 \cdot C_2H_5OH$. Recrystallization of this material from warm methanol gave orange crystals of the composition $Ni(5\text{-}Cl\text{-}TRI)(NO_3)_2 \cdot H_2O$. Evidence for the structure and composition of these compounds has been obtained from repeated elemental analyses and a comparison of infrared spectra of $Ni(TRI)(NO_3)_2 \cdot H_2O$ and these new nickel(II) complexes. The positions and intensities of the majority of the bands found in the infrared spectra of all three materials are very similar. $Ni(5\text{-}Cl\text{-}TRI)^{2+}$ has new bands at 717 cm^{-1}, which has been attributed to the C–Cl stretching vibration, and at 833 and 881 cm^{-1}, which are due to C–H out-of-plane bending modes for 1,2,5-trisubstituted benzenes.[10] The strong band at 769 cm^{-1} in the infrared spectrum of $Ni(TRI)^{2+}$ does not appear in the infrared spectrum of $Ni(5\text{-}Cl\text{-}TRI)^{2+}$ and is assigned to C–H out-of-plane bending modes for the 1,2-disubstituted benzenes. The infrared spectrum of $Ni(5\text{-}Cl\text{-}TRI)(NO_3)_2 \cdot C_2H_5OH$ shows a complex pattern between 1430 and 1450 cm^{-1} which can be assigned to an asymmetric methyl bending vibration overlapping a methylene deformation. In addition there are a number of bands of weak intensity found between 2860 and 3060 cm^{-1}, many of which do not appear in the spectrum of $Ni(5\text{-}Cl\text{-}TRI)(NO_3)_2 \cdot H_2O$. These bands have been assigned to the C–H stretching vibrations of the alkyl group. In contrast, a Nujol infrared spectrum of $Ni(5\text{-}Cl\text{-}TRI)(NO_3)_2 \cdot H_2O$ shows sharp bands at 3584, 3521, and 1650 cm^{-1} attributable to symmetric and asymmetric O–H stretching vibrations and to an H–O–H deformation mode. All infrared spectra indicate coordination of the nitrate ion to the metal.[11,12] Magnetic and absorption spectral data (Tables II and III), as well as nmr data[13] on $Ni(5\text{-}Cl\text{-}TRI)^{2+}$, compare very favorably with corresponding results obtained with $Ni(TRI)^{2+}$. The solubilities of $Ni(5\text{-}Cl\text{-}TRI)^{2+}$ in H_2O, CH_3OH, CH_3CN, etc., are not as great as those found for $Ni(TRI)^{2+}$; nevertheless, these three complexes are equally unaffected by concentrated mineral acids.[3]

TABLE II
ROOM-TEMPERATURE MAGNETIC PROPERTIES OF THE NICKEL(II) COMPLEXES

Compound	Temp, °K	$10^6\chi_M$	μ_{eff}, BM
$Ni(TRI)_2(NO_3)_2 \cdot H_2O$	302	3580	2.94
$Ni(TRI)_2I_2 \cdot H_2O$	296	3786	3.01
$Ni(TRI)_2(SCN)_2$	296	3974	3.08
$Ni(TRI)_2(PF_6)_2$	296	3938	3.07
$Ni(5\text{-}Cl\text{-}TRI)(NO_3)_2 \cdot C_2H_5OH$	296	3925	3.18
$Ni(5\text{-}Cl\text{-}TRI)(TRI)(NO_3)_2 \cdot 2H_2O$	299	4218	3.15

These results place some limitation on the manner in which the Schiff base metal chelates are formed. Apparently there is initial formation of free bis anhydro trimer and/or tris anhydro tetramer from which the Schiff base metal chelate is formed in one of two ways: (1) if an equilibrium exists between the quinazoline and the Schiff base, the metal ion may preferentially react with the more sterically favored Schiff base ligand thereby reducing its concentration and forcing the facile equilibrium in the direction of the Schiff base, or (2) the metal ion may react directly with the quinazoline inducing a rearrangement which can result in the final product. Regardless of the manner in which the Schiff base metal chelates are formed, the inductive effect of the chloro group in 2-amino-5-chlorobenzaldehyde apparently deactivates the carbonyl and amino groups on the benzene ring to such a great extent that the metal ion is not a strong enough Lewis acid to catalyze the self-condensation in contrast to the results observed with *o*-aminobenzaldehyde. Such a condensation of 2-amino-5-chlorobenzaldehyde was achieved in the presence of a strong mineral acid. The reluctance toward macrocycle formation with 2-aminoacetophenone and 2-aminobenzophenone in the presence of metal ions has also been attributed in part to the decreased reactivity of the ketonic carbonyl group thereby making formation of the bis anhydro trimer unfavorable.[14]

These metal ion induced rearrangements have been

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[10] R. T. Conley, "Infrared Spectroscopy" Allyn and Bacon, Inc., Boston, Mass., 1966.

[11] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, New York, N. Y., 1963.

[12] N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, **4**, 804 (1965).

[13] G. N. La Mar, *ibid.*, **6**, 1921 (1967).

[14] L. T. Taylor and G. A. Melson, unpublished results.

TABLE III

ELECTRONIC ABSORPTION SPECTRA[a] OF THE NICKEL(II) COMPLEXES

Compound	Medium	ν_1	ν_2	ν_3	ν_4	ν_5
$Ni(TRI)_2(NO_3)_2 \cdot H_2O$	Nujol	11,140[b]	14,300	20,000	...	...
	CH_3OH	11,300 (1.1)	14,470 (18.7)	20,200 (212)	30,800 (18,500)	36,400 (65,400)
$Ni(TRI)_2Cl_2 \cdot H_2O$	Nujol	11,700	14,500	20,120	...	...
	CH_3OH	11,300 (1.5)	14,430 (15.1)	20,240 (161)	30,800 (15,800)	36,400 (55,800)
$Ni(TRI)_2Br_2 \cdot H_2O$	Nujol	...	14,300	19,600	...	...
	CH_3OH	...	14,300 (20.8)	20,200 (217)	30,900 (18,700)	36,400 (54,000)
$Ni(TRI)_2I_2 \cdot H_2O$	Nujol	...	14,300	20,000	...	...
	CH_3OH	...	14,300 (21.7)	20,300 (213)	30,900 (18,400)	36,400 (55,000)
$Ni(TRI)_2(SCN)_2$	Nujol	...	14,300	20,000	...	...
$Ni(TRI)_2(ClO_4)_2$	Nujol	11,240	14,400	20,000	...	...
$Ni(TRI)_2(PF_6)_2$	Nujol	...	14,300	20,600	...	...
$Ni(TRI)(NO_3)_2 \cdot H_2O$	Nujol	11,000	12,400	19,400	...	...
	CH_3OH	10,800 (21.6)	12,800 (7.9)	18,400 (10.8)	31,000 (13,700)	36,200 (45,800)
$Ni(5\text{-}Cl\text{-}TRI)(NO_3)_2 \cdot C_2H_5OH$	Nujol	11,020	12,350	...	...	...
	CH_3OH	10,700 (18.3)	12,500 (8.7)	...	30,500 (10,000)	36,000 (30,500)
$Ni(5\text{-}Cl\text{-}TRI)(NO_3)_2 \cdot H_2O$	Nujol	11,170	12,500	...	...	...
	CH_3OH	10,700 (27.3)	12,500 (11.8)	...	30,500 (14,500)	36,000 (37,200)
$Ni(5\text{-}Cl\text{-}TRI)(TRI)(NO_3)_2 \cdot 2H_2O$	CH_3OH	...	14,300 (22.5)	20,300 (233)	30,900 (20,000)	36,400 (58,300)

[a] All bands given in cm^{-1}. [b] Numbers in parentheses are molar extinction coefficients.

used to synthesize a complex containing two trimeric condensates bound to each nickel(II) ion, $Ni(TRI)_2^{2+}$. This compound is prepared by heating a suspension of 2 molecular equiv of the bis anhydro trimer from *o*-aminobenzaldehyde in methanol with 1 molecular equiv of $Ni(NO_3)_2 \cdot 6H_2O$ for 2 hr. The use of methanol is critical because in ethanol $Ni(TRI)(NO_3)_2(H_2O)$ forms and is precipitated from solution. $Ni(TRI)(NO_3)_2(H_2O)$ is soluble in methanol. The red-brown material which crystallizes from the reaction mixture has the composition $Ni(TRI)_2(NO_3)_2 \cdot H_2O$. A series of derivatives has been prepared by metathetical reactions from the nitrate derivatives (see Table I). Neglecting the bands in the infrared region which can be attributed to anion or H_2O, the spectra of all derivatives are identical with the corresponding mono–trimeric condensates. In Table IV the infrared absorption bands for the iodide derivatives of $Ni(TRI)^{2+}$ and $Ni(TRI)_2^{2+}$ are listed. With regard to the perchlorate, nitrate, hexafluorophosphate, and thiocyanate derivatives, infrared spectra indicate that these anions are not coordinated to the nickel(II) ion, in contrast to the results obtained for $Ni(TRI)X_2$.[11,12,15]

Magnetic susceptibilities have been measured and magnetic moments calculated for the nitrate, iodide, thiocyanate, and hexafluorophosphate derivatives (Table II). The moment of the nitrate was measured by the Gouy method, but owing to the fibrous nature of the other compounds, which made it virtually impossible to pack them in a Gouy tube, the Faraday method had to be used. The moments are consistent with the presence of a pseudooctahedral environment about the nickel(II) ion. The six-coordinate structure is probably achieved by coordination of tridentate ligands on opposite faces of the octahedron with anions satisfying only the primary valence of nickel(II) (Figure 1).

Absorption spectra obtained on Nujol mulls and in methanol solution (when solubility permitted) were measured in the near-infrared, visible, and ultraviolet regions. The observed band maxima are tabulated in Table III. All of the spectra appear to be the same, within experimental error, indicating that the metal ion environment is common for all salts, both in solution and in the solid state. The noncoordination of anions is supported by the observation that in methanol solution the derivatives behave as 2:1 electrolytes (Table V). In some cases the positions of the absorption maxima were difficult to determine because all of the

TABLE IV

INFRARED SPECTRA[a] OF THE NICKEL(II) COMPLEXES CONTAINING TRIMERIC CONDENSATES OF *o*-AMINOBENZALDEHYDE (CM^{-1})

$Ni(TRI)I_2(H_2O)$	Assignment	$Ni(TRI)_2I_2 \cdot H_2O$
3550 m	O—H str	...
3400 m	O—H str	3448 m, b
3230 m, b	O—H str	...
3035 vw	C—H str	3012 w
2900 vw	C—H str	2910 vw
1650 w, sh	H—O—H def	1653 w, sh
1620 vs	C_6 ring I	1618 vs
1592 s	C_6 ring II	1592 s
1569 s	C=N str	1569 s
1488 m	C_6 ring III	1488 m
1441 m	C_6 ring IV	1445 m
1372 m	...	1377 m
1300 m	...	1302 w
1272 w	...	1278 w
1237 m	...	1236 m
1189 ms	...	1189 m
1161 sh	...	1164 w, sh
1110 m	...	1114 w
975 m	...	976
914 m	...	917 m
855 w	...	851 m
800 w	...	800 w
769 vs	C—H def	763 vs
541 w	...	542 m
506 m	...	500 s
455 w, b	...	450 w, b
410 w, b	...	410 m, b

[a] Abbreviations used: b, broad; m, medium; sh, shoulder; s, strong; w, weak; v, very.

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(15) N. F. Curtis and Y. M. Curtis, *Australian J. Chem.*, **19**, 1423 (1966).

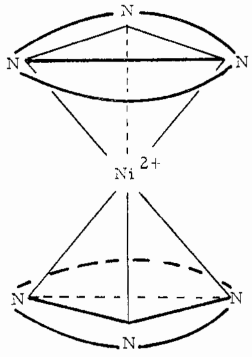


Figure 1.

TABLE V
MOLAR CONDUCTANCES FOR SALTS OF $Ni(TRI)_2^{2+}$ AT ROOM TEMPERATURE IN METHANOL

Compound	[Complex], m*M*	λ_M, ohm^{-1} cm^{-2} mol^{-1}
$Ni(TRI)_2(NO_3)_2 \cdot H_2O$	1.05	157
$Ni(TRI)_2Cl_2 \cdot H_2O$	0.909	164
$Ni(TRI)_2Br_2 \cdot H_2O$	0.960	159
$Ni(TRI)_2I_2 \cdot H_2O$	0.919	163

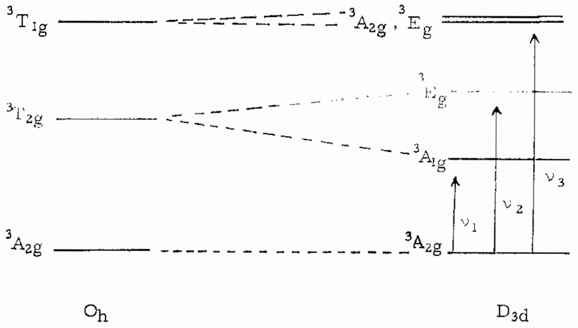
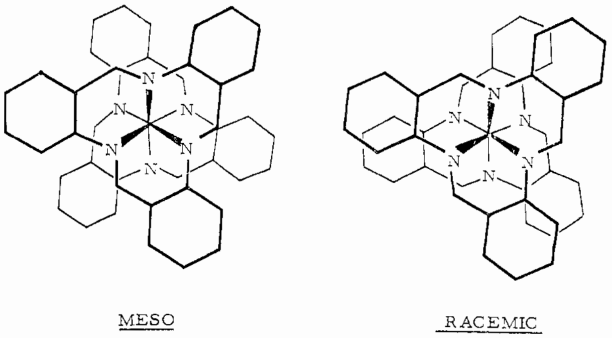


Figure 2.—Electronic absorption bands of $Ni(TRI)_2^{2+}$.



MESO RACEMIC

Figure 3.—The two possible geometrical arrangements of $Ni(TRI)_2^{2+}$.

bands appear as broad shoulders. The unusually high intensity of the third band (for nickel(II) in an octahedral environment) is no doubt due to the charge-transfer band at 30,800 cm^{-1}. The spectra have been interpreted assuming the effective symmetry of the complex is D_{3d}, since strong trigonal distortion from O_h symmetry is evident in the structure. The absorption bands in the visible region have been assigned as shown in Figure 2. Electronic transitions involving the Schiff base ligands give rise to ν_4 and ν_5. This is evidenced by the observation that the uv spectra of $Ni(TRI)^{2+}$ and $Ni(TRI)_2^{2+}$ are essentially identical except for a much higher extinction coefficient for $Ni(TRI)_2^{2+}$.

Successful resolution of $Ni(TRI)(H_2O)_3^{2+}$ [16] into optical isomers has prompted us to investigate the stereochemistry of complexes of $Ni(TRI)_2^{2+}$. Figure 3 shows two geometrical arrangements for these complexes based on the relative clockwise or counterclockwise progression of the repeating unit (carbon, benzene, nitrogen or carbon, nitrogen, benzene) in each macrocyclic Schiff base moiety. The isomer that has the benzene rings staggered belongs to the S_6 point group and is properly identified as the *meso* form. The second isomer belongs to the D_3 point group and will be termed the racemic form. Attempts to separate these microscopically homogeneous complexes into two forms by chromatographic techniques have not been successful. The identical ultraviolet spectra of $Ni(TRI)^{2+}$ and $Ni(TRI)_2^{2+}$ (see Table III) and the improbably low nonbonded distance between benzene rings of 2.8 Å as predicted from Drieding stereomodels appears to militate against formation of the racemic form. On the other hand, the minimum nonbonded distance between benzene rings in the *meso* form is 3.5 Å. The *meso* form also has benzene rings in a staggered conformation; therefore, we believe $Ni(TRI)_2^{2+}$ exists solely in this more sterically favored *meso* form.

In order to prove our hypothesis, partially resolved $Ni(TRI)(NO_3)_2(H_2O)$ was caused to react with 1 molar equiv of $(oab)_3$ and the rotation of the product was determined. The possible products are shown schematically in Figure 4. If we assume that the resolved $Ni(TRI)^{2+}$ has the repeating carbon, nitrogen, benzene unit progressing in such a way that we may call it the *d* isomer, then it is clear that the second trimeric Schiff base ligand may coordinate to the nickel ion such that the repeating unit progresses either counterclockwise or clockwise thereby generating either a *meso* (one *d*- and one *l*-TRI) or an optically active form (two *d*-TRI). (See also Figure 3.) A random or exclusive attachment of *d*-TRI would result in an optically active product since we began with partially resolved starting material. However, if the ligand is required to coordinate in such a way that the nonbonded distance between benzene rings is maximized, the two ligands have opposite configurations and only the *meso* form is produced and the product should exhibit no rotation. During this reaction we must assume that the Ni-

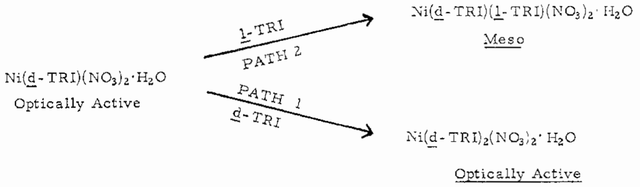


Figure 4.—Schematic representation of the possible products obtainable from the reaction of partially resolved $Ni(TRI)(NO_3)_2 \cdot H_2O$ with the bis anhydro trimer of *o*-aminobenzaldehyde.

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[16] L. T. Taylor and D. H. Busch, *J. Am. Chem. Soc.*, **89**, 5372 (1967).

$(TRI)^{2+}$ does not racemize. This is probably a fair assumption in light of the extreme inertness to dissociation and racemization found for this material.

The $Ni(TRI)_2^{2+}$ produced from partially resolved $Ni(TRI)^{2+}$ has no observable rotation. Therefore, the $Ni(TRI)_2^{2+}$ exists in only the *meso* form, and the reaction shown in Figure 4 proceeds stereospecifically (by path 1).

Efforts to prepare $Ni(TRI)(5\text{-}Cl\text{-}TRI)(NO_3)_2$ by the reaction of resolved $Ni(TRI)^{2+}$ with the bis anhydro trimer of 2-amino-5-chlorobenzaldehyde under numerous conditions have thus far failed indicating again the less reactive properties of the chloro derivative.[17] On the other hand, the more reactive $(oab)_3$ does rearrange in the presence of $Ni(5\text{-}Cl\text{-}TRI)(NO_3)_2(C_2H_5OH)$ or $Ni(5\text{-}Cl\text{-}TRI)(NO_3)_2(H_2O)$ to give $Ni(5\text{-}Cl\text{-}TRI)(TRI)(NO_3)_2 \cdot H_2O$. Evidence for the composition of this compound has been obtained primarily from elemental analyses and infrared spectra. In Table VI several infrared absorption bands for $Ni(5\text{-}Cl\text{-}TRI)(TRI)(NO_3)_2 \cdot 2H_2O$ are listed and compared with corresponding infrared absorption bands for $Ni(TRI)(NO_3)_2(H_2O)$ and $Ni(5\text{-}Cl\text{-}TRI)(NO_3)_2(H_2O)$. It can be seen that $Ni(5\text{-}Cl\text{-}TRI)(TRI)(NO_3)_2 \cdot 2H_2O$ has bands characteristic of both chloro- and unsubstituted trimeric condensates. The magnetic moment, absorption spectrum, and physical and chemical properties for this material suggest a structure analogous to $Ni(TRI)_2(NO_3)_2(H_2O)$ (see Tables II and III) which probably exists in the isomeric form with its benzene rings in a staggered conformation.

TABLE VI

INFRARED SPECTRA[a] OF THE NICKEL(II) COMPLEXES CONTAINING CHLORO- AND UNSUBSTITUTED TRIMERIC CONDENSATES OF *o*-AMINOBENZALDEHYDE

Assignment	$Ni(TRI)(NO_3)_2 \cdot H_2O$	$Ni(5\text{-}Cl\text{-}TRI)(TRI)(NO_3)_2 \cdot 2H_2O$	$Ni(5\text{-}Cl\text{-}TRI)(NO_3)_2 \cdot H_2O$
C_6 ring I	1620 vs	1617 vs	1621 vs
C_6 ring II	1592 s	1590 m	1590 m
C=N str	1569 s	1565 m	. . .
C=N str	. . .	1558 m	1560 m
C_6 ring III	1488 m	1484 s	1484 s
C_6 ring IV	1441 m	1441 m	1443 m
C—H def	. . .	881 w	881 m
C—H def	. . .	833 s	833 vs
C—H def	769 vs	781 s	. . .
C—Cl str	. . .	717 m	720 s

[a] Abbreviations used: b, broad; s, strong; m, medium; w, weak; v, very.

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[17] Regardless of the manner in which the chloro-Schiff base had coordinated to the $Ni(TRI)^{2+}$, the resulting product would have been asymmetric and if racemization had not occurred, the product would have had an observable rotation.

Notes

CONTRIBUTION FROM THE INSTITUTE OF CHEMISTRY,
UNIVERSITY OF TURIN, TURIN, ITALY

Isotopic Exchange Reactions of Carbon Monoxide with Rhenium Pentacarbonyl Halides

BY G. CETINI, O. GAMBINO, G. A. VAGLIO, AND R. P. FERRARI

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A considerable number of studies on the behavior of metal carbonyls in exchange and substitution reactions have appeared in recent years. These have been directed to the collection of data on compound reactivity *via* such parameters as coordinator element type, degree of substitution of CO groups, and so on. Some excellent papers on this subject have already appeared.[1,2]

Our previous studies were concerned with the exchange reaction behavior of metal carbonyls containing elements of groups VI and VIII of the periodic table, in particular Cr, Mo, and W carbonyls[3-5] and Fe, Ru, and Os tricarbonyls.[6,7] The present paper reports CO isotopic exchange reactions with rhenium pentacarbonyl halides; data dealing with similar reactions involving technetium pentacarbonyl halides are being prepared for publication in a separate work.

Previous studies carried out with $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ had met with little success. When light was excluded, the exchange rate was very slow and the behavior of photochemical reactions could not be accurately determined.

Our present results are compared with already published data dealing with exchange[8,9] and substitution[10] reactions involving compounds of the $Mn(CO)_5X$ type

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[10] R. J. Angelici and F. Basolo, *J. Am. Chem. Soc.*, **84**, 2495 (1962).