position of tropenium ion. The value of $\Delta H°_{(4)}$ for the formation of tropenium hydrogen dibromide is greater than can be accounted for by cation size alone.

The entropy of complex salt formation, $\Delta S°_{(4)} = \Delta S°_{(L)} + \Delta S°_{(1)}$, is negative; the differential lattice entropy $\Delta S°_{(L)}$ might be either positive or negative (although it is probably negative for ions of as low symmetry as the hydrogen dihalides), but $\Delta S°_{(1)}$ is large and negative and probably contributes the most weight to the entropy term. Consideration of our data shows that the formation of tropenium hydrogen dibromide is hindered by entropy to a greater extent than that of the other salts studied. Examination of Table II will show that, relative to tetramethylammonium hydrogen dibromide, the tetraethylammonium salt is favored by both enthalpy and entropy factors, while the tropenium salt is favored by enthalpy and hindered by entropy. The greater stability of tetraethylammonium hydrogen dibromide over the tropenium salt comes entirely from entropy factors.

The net result of this entropy discussion is that $\Delta S°_{(L)}$ for the formation of tropenium hydrogen dibromide is more negative (or, perhaps, less positive) than for the other salts; this indicates a higher degree of ordering of the anions in the lattice of the tropenium complex salt. Crystals of tropenium hydrogen dibromide are a bright yellow (somewhat lighter in shade than the bromide), and thus charge-transfer processes are taking place in the solid. It seems possible that the existence of a weak transfer bond, such as has been postulated in crystalline tropenium iodide,[41] could result in more stringent requirements on anion position in the tropenium salt and account for the entropy effects noted.

The unusually low value of $\Delta H°_{(L)}$ for the formation of the tropenium salt is not easily accounted for. The ion has a different shape and polarizability than the tetraalkylammonium ions but is presumably similar in shape and polarizability to the pyridinium ion which does not show this marked effect. The most obvious different feature of the tropenium ion is its delocalized positive charge; the other three ions studied have a point unit of positive charge centered on the nitrogen nucleus, while in the tropenium ion the charge is distributed by resonance throughout the whole cation. Exactly how this delocalization of charge could produce the observed effect is certainly not clear at this time; however, in the first approximation the coulombic attraction between two diffusely charged nonspherical objects is greatest when they are of the same size, and tropenium ion salts of large anions may be stabilized by this effect. Further speculation should wait on further evidence, such as the examination of salts of other delocalized cations and investigation of the effect of the extent of delocalization of charge in the anion.

In conclusion, tropenium hydrogen dibromide is stabilized by a low positive value of $\Delta H°_{(L)}$ which outweighs adverse entropy effects and which cannot be accounted for by the ion's size. We believe that this effect may be even more marked in the tetrahaloborate salts where both absence of charge-transfer bonding and higher anion symmetry should reduce adverse entropy effects. Vapor pressure measurements on tropenium and tetraalkylammonium haloborates are in progress.

Reactions of Coordinated Ligands. XI. The Formation and Properties of a Tridentate Macrocyclic Ligand Derived from o-Aminobenzaldehyde

Gordon A. Melson[1] and Daryle H. Busch

Contribution from the Evans and McPherson Chemical Laboratories, The Ohio State University, Columbus, Ohio. Received November 20, 1964

The self-condensation of o-aminobenzaldehyde in the presence of nickel(II) ions has been shown to produce a closed tridentate macrocyclic ligand, tribenzo[b,f,j][1.5.9]triazacycloduodecine (TRI), in addition to the previously described tetradentate macrocyclic ligand. The resultant complexes exhibit pseudo-octahedral stereochemistry with the three donor nitrogen atoms of the macrocycle occupying one face of the octahedron. The other positions are occupied by a water molecule and two unidentate anions, or by water molecules alone, in the series of compounds of the composition Ni(TRI)-$X_2 \cdot nH_2O$, where n is one in all cases except for the

tetraphenylborate salt. The reaction to produce these cyclic ligands is assumed to include the metal ion acting as a template for the condensation. Although a tridentate macrocycle does not enclose the metal ion in the usual sense, this complex ion is remarkably stable toward ligand displacement in concentrated acids.

Introduction

Recently, several reactions have been reported in which metal ions serve as templates, thereby directing the steric course of the process and leading to the synthesis of species not readily obtained in the absence of the metal ion. A number of these reactions have
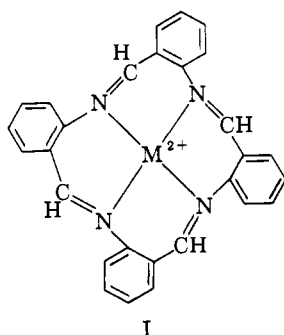
(1) Department of Chemistry, University of Strathclyde, Glasgow, Scotland.

Table I. Analytical Data for the Nickel(II) Complexes of the Tridentate Macrocycle TRI
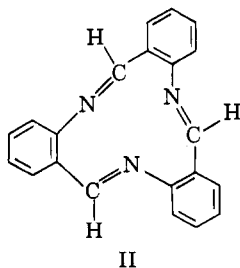
Compound	Calculated, %					Found, %				
	C	H	N	Halogen	S	C	H	N	Halogen	S
Ni(TRI)H₂O(ClO₄)₂	43.08	2.90	7.18	12.12	...	43.57	4.33	7.21	10.96	...
Ni(TRI)H₂O(BF₄)₂	45.00	3.04	7.50	27.14	...	45.17	3.28	7.61	27.10	...
Ni(TRI)(H₂O)₃[B(C₆H₅)₄]₂	78.14	5.80	3.96	...	...	77.11	6.05	4.32	...	...
Ni(TRI)H₂OBr₂	46.15	3.11	7.64	29.30	...	46.41	3.09	7.64	29.47	...
Ni(TRI)H₂OI₂	39.37	2.66	6.56	39.72	...	39.75	3.24	6.58	40.35	...
Ni(TRI)H₂O(NO₃)₂	49.44	3.34	13.72	...	...	49.66	3.48	13.75	...	...
Ni(TRI)H₂O(SCN)₂	54.98	3.38	13.94	...	12.72	54.83	3.42	13.70	...	12.57

resulted in the formation of macrocyclic organic ligands which have generally been isolated in the form of their complexes with the templating metal ion.

The majority of these examples have produced closed tetradentate macrocyclic ligand systems coordinated in a plane about the metal atom.[2-8] In addition, Curry and Busch[9] synthesized penta- and hexadentate macrocyclic chelate ligands by the reaction of 2,6-diacetylpyridine with linear aliphatic polyamines in the presence of an iron salt. We have previously shown that the self-condensation of o-aminobenzaldehyde in the presence of nickel(II) and copper(II) ions produces a closed tetradentate macrocyclic ligand tetrabenzo[b,f,j,n][1.5.9.13]-tetraazacyclohexadecine (structure I), the four donor nitrogen atoms coordinating to the metal atom in a planar manner.[10, 11]

I

A second product isolated from the condensation in the presence of nickel(II)[10] has now been characterized

II

as a closed tridentate macrocyclic ligand, tribenzo-[b,f,j][1.5.9]triazacycloduodecine (II), denoted as TRI.[12] This report describes the isolation, characterization, and properties of the nickel(II) complexes containing this first tridentate macrocyclic ligand to be produced via a ligand reaction.

Experimental

Materials. o-Aminobenzaldehyde was prepared by the method described by Smith and Opie.[13] All other chemicals were obtained commercially and were of reagent grade or equivalent.

Isolation of Diperchloratoaquotribenzo[b,f,j][1.5.9]-triazacycloduodecinenickel(II) [Ni(TRI)H₂O(ClO₄)₂]. The experimental details for the reaction of o-aminobenzaldehyde with nickel(II) nitrate and the isolation of the orange solid product have previously been described.[11] The addition of a concentrated aqueous solution of sodium perchlorate to an aqueous solution of this material (2.0 g. in approximately 200 ml.) immediately produces a bright red precipitate of the previously described Ni(TAAB)(ClO₄)₂ (1.0 g.). The solution is filtered and the filtrate concentrated on a rotary evaporator. A yellow crystalline precipitate is produced. This is isolated by filtration, washed with water, and dried *in vacuo* over anhydrous Mg(ClO₄)₂ at room temperature; yield of Ni(TRI)H₂O(ClO₄)₂, 0.8 g.

Preparation of Other Derivatives of the Tribenzo-[b,f,j][1.5.9]triazacycloduodecinenickel(II) Group. To a saturated solution of the perchlorate salt in water (approximately 1.0 g. in 100 ml.) at room temperature is added about 10 ml. of a concentrated aqueous solution of the sodium salt of the required anion together with a few drops of the corresponding acid, where available. In the cases of thiocyanate, fluoroborate, and tetraphenylborate, the salts are precipitated immediately. The bromide, iodide, and nitrate salts crystallize on standing overnight at room temperature. All products are isolated with suction filtration, washed with water, and dried *in vacuo* at room temperature over anhydrous Mg(ClO₄)₂. Using this procedure, the yield of the metathetical product is almost quantitative. All products are deep yellow in color. Analytical data are recorded in Table I.

Magnetic Measurements. Magnetic measurements were made by the Gouy method. The susceptibilities

(2) M. C. Thompson and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 3651 (1964).
(3) M. C. Thompson and D. H. Busch, *ibid.*, **86**, 213 (1964).
(4) D. A. House and N. F. Curtis, *ibid.*, **84**, 3248 (1962).
(5) D. A. House and N. F. Curtis, *ibid.*, **86**, 223 (1964).
(6) D. A. House and N. F. Curtis, *ibid.*, **86**, 1331 (1964).
(7) G. N. Schrauzer, *Chem. Ber.*, **95**, 1438 (1962).
(8) D. Thierig and F. Umland, *Angew. Chem.*, **74**, 388 (1962).
(9) J. D. Curry and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 592 (1964).
(10) G. A. Melson and D. H. Busch, *Proc. Chem. Soc.*, 223 (1963).
(11) G. A. Melson and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 4834 (1964).

of ligands and anions were calculated from Pascal's constants.[14] The standard used was HgCo(NCS)$_4$.

Infrared Spectra. Infrared absorption spectra were obtained using a Perkin-Elmer Model 337 recording spectrophotometer. Nujol mull and potassium bromide pellet techniques were employed. Polystyrene was used for calibration.

Reflectance Spectra. Reflectance spectra were obtained with a Cary Model 14 recording spectrophotometer and a diffuse reflectance attachment.

Analyses. Analyses were performed by the Schwarzkopf Microanalytical Laboratories.

Results and Discussion

The self-condensation of *o*-aminobenzaldehyde in the presence of nickel(II) ion yields two cationic complexes, one containing a ligand composed of 4 moles of the self-condensed aldehyde bound to a metal ion, the other containing a ligand composed of 3 moles of the self-condensed aldehyde bound to a metal ion. For the trimeric condensate (TRI), the following series of compounds has been isolated by metathetical reactions: [Ni(TRI)H$_2$O(ClO$_4$)$_2$], [Ni(TRI)H$_2$O(BF$_4$)$_2$], [Ni(TRI)-(H$_2$O)$_3$][B(C$_6$H$_5$)$_4$]$_2$, [Ni(TRI)H$_2$O(Br)$_2$]. [Ni(TRI)-H$_2$O(I)$_2$], [Ni(TRI)H$_2$O(NO$_3$)$_2$], and [Ni(TRI)H$_2$O-(SCN)$_2$]. These compounds have been identified and characterized as complexes of the fully cyclized ligand tribenzo[*b*,*f*,*j*][1.5.9]triazacycloduodecine (II) by elemental analyses, infrared spectra, magnetic moments, and electronic reflectance spectra. The analytical data are recorded in Table I. In addition to the tridentate ligand, each compound contains one molecule of water associated with the complex as a whole, excepting the tetraphenylborate which contains 3 moles of water.

The room temperature magnetic properties are recorded in Table II. In all cases the moment is

Table II. Room Temperature Magnetic Properties of the Nickel(II) Complexes

Compound	Temp., °K.	$\chi_M \times 10^6$	μ_{eff}, B.M.
Ni(TRI)H$_2$O(ClO$_4$)$_2$	300	3910	3.20
Ni(TRI)H$_2$O(BF$_4$)$_2$	300	4060	3.24
Ni(TRI)(H$_2$O)$_3$[B(C$_6$H$_5$)$_4$]$_2$	299	4250	3.30
Ni(TRI)H$_2$OBr$_2$	300	3630	3.08
Ni(TRI)H$_2$OI$_2$	300	4120	3.24
Ni(TRI)H$_2$O(NO$_3$)$_2$	301	4080	3.24
Ni(TRI)H$_2$O(SCN)$_2$	299	3960	3.18

consistent with the presence of a pseudo-octahedral environment about the nickel(II), resulting in a triplet ground state. This octahedral environment is achieved by the coordination of the tridentate ligand on one face. One molecule of water and the two anions, X, occupy the other three positions (III). Models indicate this to be the only possible mode of attachment of the organic ligand. In the case of a noncoordinating anion, *e.g.*, tetraphenylborate, the complex contains

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

two additional water molecules in the positions where the anions are otherwise bound to the metal ion.

III
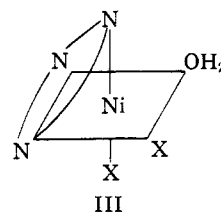
Evidence for the structure and composition of the compounds has been obtained from the infrared spectra. In Table III the infrared absorption bands

Table III. Infrared Spectra of the Nickel(II) Complexes Containing Trimeric and Tetrameric Condensates of *o*-Aminobenzaldehyde

Ni(TRI)-H$_2$O (I)$_2$[a]	Assignment	Ni(TAAB)-I$_2$[a]
3550 m	O–H st.	...
3400 m	O–H st.	...
3230 mb	O–H st.	...
3035 vw	C–H st.	3020 vw
2900 vw	C–H st.	2925 vw
1650 wsh	H–O–H bend	...
1620 vw	C$_6$–ring I	1610 vw
1592 s	C$_6$–ring II	1589 s
1569 s	C=N st.	1568 vs
1488 m	C$_6$–ring III	1492 m
1441 m	C$_6$–ring IV	1441 m
1372 m		1404 s
1300 m		1319 m
1272 w		1282 m
1237 m		1239 wb
1189 ms		1198 s
1161 sh		1173 sh
1110 m		1122 m
975 m		985 m
914 m		923 m
855 w		824 m
800 w		...
769 vs	C–H def.	780 s
...	C–H def.	765 s
541 w		595 w
506 m		532 w
455 wb		494 vb
410 wb		472 wb

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

for the iodide derivative Ni(TRI)H$_2$OI$_2$ are listed and compared with the iodide salt of the corresponding tetrameric condensate Ni(TAAB)I$_2$. It can be readily seen that the two ligand structures are closely related to each other. The positions and intensities of the majority of the bands are very similar as expected if the two ligand structures differ only in the number of repeating units in the cycle. In both compounds, the absence of stretching and deformation frequencies for the NH$_2$ group, the absence of the >C=O stretching frequency, and the presence of a strong band at 1568 cm.$^{-1}$, assigned to the stretching mode of the conjugated, coordinated C=N group, provide strong evidence for the existence of closed macrocycles containing Schiff base linkages. The intensity of the >C=N– stretching mode in the trimeric condensate is

somewhat less, relative to other bands, than that of the tetrameric condensate. This is the most striking difference in the two spectra. The largest differences between the two spectra occur in the low energy region below 600 cm.$^{-1}$, where effects due to the metal–ligand frequencies are important and the difference in ring size and in the stereochemistry of the metal should be of maximum significance. The infrared spectrum of the ligand remains unchanged for the different derivatives of the tridentate macrocycle.

In agreement with structure III, all compounds show a broad absorption band corresponding to the OH stretching vibrations of the water molecules between 3600 and 3300 cm.$^{-1}$ and the H–O–H bending mode at 1650 cm.$^{-1}$. These absorptions are much stronger and sharper in the tetraphenylborate salt, sharp bands of medium intensity being observed at 3630, 3520, 3490, and 3440 cm.$^{-1}$.

Structure III also requires that the anions be coordinated. Infrared spectra of the compounds confirm the coordination of the anions in the cases of the perchlorate, nitrate, and thiocyanate. For the perchlorate, two very strong bands are observed, in the Nujol mull spectrum, at 1110 and 1080 cm.$^{-1}$, together with one of medium intensity at about 960 cm.$^{-1}$. The lower frequency absorption also occurs as two bands at 650 and 624 cm.$^{-1}$. From previous reports of perchlorate coordination[15,16] and by analogy with sulfato complexes,[17] these absorptions are characteristic of a change from T_d to C_{3v} symmetry for the perchlorate functioning as a unidentate ligand. When the spectrum is run using a potassium bromide pellet, the 960-cm.$^{-1}$ band is considerably reduced in intensity and the splitting of the 650–624-cm.$^{-1}$ band is reduced to the point where a shoulder occurs at 640 cm.$^{-1}$ on the 624-cm.$^{-1}$ band, indicating some interaction with the KBr to produce unbound perchlorate. The nitrate spectra, both that obtained on a Nujol mull and with a potassium bromide pellet, show strong bands at 1430 and 1295 cm.$^{-1}$ and a band of medium intensity at 1040 cm.$^{-1}$. These features indicate unidentate coordination of the nitrate ion to the metal.[18,19] The thiocyanate shows a strong–C≡N– absorption at 2078 cm.$^{-1}$ with a shoulder at 2115 cm.$^{-1}$, suggesting coordination through the nitrogen atom. No absorption due to the C–S stretching mode could be assigned, but the N–C–S bending mode was observed as a band of medium intensity at 471 cm.$^{-1}$. The spectrum was identical in Nujol and a potassium bromide pellet. The fluoroborate shows a very intense broad band at about 1060 cm.$^{-1}$ and a band of medium intensity at 520 cm.$^{-1}$ in a Nujol mull. As was observed by others,[16] it does not appear that the infrared spectrum of the fluoroborate ion will be as helpful in deciding whether or not that ion is coordinated. From analytical data, it is assumed that the fluoroborate is functioning as a unidentate ligand in the manner observed for perchlorate. Similarly, iodide and bromide are presumed to be coordinated to the nickel atom.

(15) L. E. Moore, R. B. Gayhart, and W. E. Bull, *J. Inorg. Nucl. Chem.*, **26**, 896 (1964).
(16) S. Buffagni, L. M. Vallarino, and J. V. Quagliano, *Inorg. Chem.*, **3**, 671 (1964).
(17) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 164.
(18) C. C. Addison and B. M. Gatehouse, *J. Chem. Soc.*, 613 (1960).
(19) P. C. H. Mitchell and R. J. P. Williams, *ibid.*, 613 (1960).

The reflectance spectra of the compounds were measured over the range from 7400 to 33,000 cm.$^{-1}$ and are recorded in Table IV. All showed the four

Table IV. Reflectance Spectra[a] of Nickel(II) Complexes of TRI

Compound	ν_1	ν_2	ν_3	ν_4
Ni(TRI)H$_2$O(ClO$_4$)$_2$	10,410	12,500	18,200	25,600
Ni(TRI)(H$_2$O)$_3$[B(C$_6$H$_5$)$_4$]$_2$	10,890	12,820	18,500	25,000
Ni(TRI)H$_2$OBr$_2$	10,750	12,900	18,900	25,000
Ni(TRI)H$_2$OI$_2$	10,520	11,500	18,200	25,600
Ni(TRI)H$_2$O(NO$_3$)$_2$	10,700	12,680	18,700	25,000
Ni(TRI)H$_2$O(SCN)$_2$	10,810	12,720	19,020	25,000
Ni(TRI)H$_2$O(ClO$_4$)$_2$ (in water)	10,890 (ϵ 16.5)	12,900 (ϵ 6.4)	...	...

[a] All bands given in cm.$^{-1}$.

bands expected for octahedral nickel(II) species and, therefore, the spectral results are consistent with the magnetic moments. The absorption bands have been assigned to the following transitions in (pseudo) O_h symmetry: ν_1, $^3A_{2g} \rightarrow \,^3T_{2g}$; ν_2, $^3A_{2g} \rightarrow \,^1E_g$; ν_3, $^3A_{2g} \rightarrow \,^3T_{1g}(F)$; ν_4, $^3A_{2g} \rightarrow \,^3T_{1g}(P)$ (plus charge transfer). Assuming the ligand field due to the tridentate ligand and the coordinated water molecule remains constant throughout the series of compounds, the observed order of increasing ligand field strength gives the following spectrochemical series for the coordinated anions: $ClO_4^- < I^- < NO_3^- \sim Br^- < NCS^- \sim H_2O$. This is in agreement with the usual spectrochemical series[20] and demonstrates the rule of average environment.[21]

It is interesting to note that the reflectance spectrum of the tetraphenylborate salt, which has been assumed to contain three molecules of coordinated water and the tridentate ligand, is very similar to the spectrum of an aqueous solution of the perchlorate compound, in which we assume the perchlorate anions are replaced by water molecules. In spite of the uncertainty of the positions of the ν_3 and ν_4 bands (ν_3 occurs as a shoulder on the intense broad ν_4 absorption), the parameters $15B$ and β_1, in Jørgensen's notation,[21] were calculated for each derivative. These values are comparable in magnitude to those of most octahedral or tetragonal nickel(II) compounds. However, because of the previously mentioned uncertainty in band positions, the actual numerical values are of little quantitative value.

These compounds, like those containing the corresponding tetradentate macrocycle, are very stable toward mineral acids. They are not decomposed in concentrated hydrochloric, nitric, or perchloric acid, but merely undergo metathesis. Unlike macrocyclic tetra-, penta-, and hexadentate ligands, the tridentate molecule of immediate concern does not essentially *enclose* the metal ion. In fact, it almost certainly resides on a single face of the coordination polyhedron. It follows that the insensitivity of the nickel complex, Ni(TRI)(H$_2$O)$_3^{2+}$, toward dissociation in strong acid cannot be ascribed to the inability of the metal ion to escape from an enclosing macrocycle. Certainly, it is

(20) Reference 14, p. 266.
(21) O. Bostrup and C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 1223 (1957).

well understood that nickel(II) complexes of such strong ligands as dipyridyl dissociate only slowly in strongly acidic media. However, $Ni(TRI)(H_2O)_3{}^{2+}$ appears to be much less reactive than, for example, $Ni(dipy)(H_2O)_4{}^{2+}$, for which the dissociation half-life is a few hours in the vicinity of room temperature.[22] This extreme unreactivity of the complex of the cyclic tridentate ligand may be attributed to the absence of terminal donor groups in the ligand; i.e., coordinated groups that might first dissociate and protonate and, in this way, initiate and perpetuate the stepwise dissociation of the ligand.

The coordinated ligand is sensitive to base. The reaction appears to involve the addition of water molecules across the Schiff base linkages to produce α-carbinolamines, in the manner observed for the similar tetradentate macrocycle.[11]

The compounds containing the tridentate ligand and those containing the tetradentate ligand behave differently toward ethylenediamine. The addition of an aqueous solution of ethylenediamine to an aqueous solution of the nickel complex of the tetradentate ligand, $Ni(TAAB)^{2+}$, results in the formation of the same product isolated from the reaction with hydroxide ion. However, for the tridentate derivative, $Ni(TRI)(H_2O)_3{}^{2+}$ (as perchlorate), a brown solid is precipitated on the addition of an aqueous solution of ethylenediamine. The infrared spectrum of this brown solid shows the presence of ethylenediamine in addition to water and the trimeric ligand. The perchlorate anions have infrared absorptions characteristic of the ionic form. It seems most probable that an ethylenediamine molecule has displaced the anions from their cis positions in the coordination sphere in this product.

The mechanisms of formation of both the trimeric and tetrameric macrocycles are of considerable interest and must serve to illustrate the template influence of the metal ion.[2,23] The point of particular concern

(22) P. Ellis, R. Hogg, and R. G. Wilkins, J. Chem. Soc., 3308 (1959).

derives from the fact that the number of o-aminobenzaldehyde units cyclopolymerized depends on the metal ion. In the case of copper(II) ion,[11] only the cyclic tetramer is generated (as its Cu(II) complex). In contrast, as shown here, the reaction with nickel(II) ion leads to both the cyclic tetramer and a cyclic trimer (as their Ni(II) complexes). Comment has been offered on the general nature of the process earlier.[11,23] Most reasonably it is assumed that, as the o-aminobenzaldehyde condenses with itself, each intermediate polymeric ligand is bound to the metal ion. The self-condensation is assumed to proceed stepwise, in this fashion, until the terminal reactive groups (an NH_2 and a $CH=O$ group) are sufficiently close in proximity to permit final ring closure. Obviously, if a metal ion confines the donor atoms of such intermediates to an encircling plane, as in a square-planar coordination sphere, a tetrameric, tetradentate macrocycle must be produced. However, if the intermediates can bind along as many as three mutually cis positions (structure IV), then a trimeric, tridentate macrocycle may form. Clearly, metal ions that bind donor groups more firmly in a fourfold planar array should favor the cyclic tetramer (Cu(II)) while those of octahedral coordination spheres may produce both the tetramer and the cyclic trimer (Ni(II)).
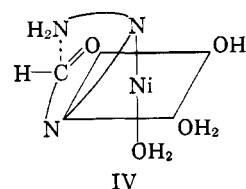
IV

(23) D. H. Busch, Record Chem. Progr. (Kresge-Hooker Sci. Lib.), 25, 107 (1964).

Reactions of the Uranium Carbides with Nitric Acid[1]

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Contribution from the Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee. Received December 3, 1964

The uranium carbides reacted with 2 to 16 M HNO_3 at 25 to 120° yielding uranyl nitrate, soluble organic acids, NO_2, NO, and CO_2. No hydrogen, CO, or gaseous hydrocarbons were produced. Between 50 and 80% of the carbide carbon was converted to CO_2. The soluble organic species consisted of oxalic acid (0 to 11% of the carbide carbon), mellitic acid (2 to 9% of the carbide carbon), and unidentified compounds which were probably aromatics highly substituted with –COOH and –OH groups. The carbides were practically passive in boiling 0.001 to 0.5 M HNO_3.

Introduction

Several prior investigations of the reactions of the uranium carbides with nitric acid have been conducted, each giving somewhat different results. Simpson and Heath[2] studied the reaction of the monocarbide with 6 M HNO_3. Carbon-containing compounds were not found in the off-gas, so they concluded that all of the carbide carbon remained in the solution. The dark brown color of the solution was attributed to materials similar to the "humic" acids produced by oxidation of

(2) A. M. Simpson and B. A. Heath, UKAEA Report IG Memorandum 464(D), June 1959.