general implication of all the present results for cobalt(III)–amine substitution reactions is now being explored.

Registry No. $(NH_3)_5CoO{=}SMe_2^{3+}$, 44915-85-7; Cl_2, 7782-50-5; $[(NH_3)_5CoOClO_3](ClO_4)_2$, 18042-14-3; $[(NH_3)_5CoOClO_3](NO_3)_2$, 56335-61-6; $[(NH_3)_5CoN_3](ClO_4)_2$, 14283-04-6.

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(2) P. J. Cresswell, Ph.D. Thesis, Australian National University 1974. The value there obtained for the rate constant was 2.7×10^{-2} sec^{-1} (25°, $I = 1.0$, $NaClO_4$).

(3) The synthesis of the perchlorato complex has been reported previously by R. Duval, *Ann. Chim. (Paris)*, **18**, 241 (1932), but the properties given (see also R. Duval, C. Duval, and J. Lecomte, *Bull. Soc. Chim. Fr.*, 1048 (1947)) do not coincide with those presently described. We have been unable to obtain any solid other than $[(NH_3)_5CoOH_2](ClO_4)_3$ by Duval's synthetic procedure.

(4) Similar, though less well resolved, ir absorptions are seen for the complex $Co(DTH)_2(ClO_4)_2$ (DTH = 2,5-dithiahexane): F. A. Cotton and D. L. Weaver, *J. Am. Chem. Soc.*, **87**, 4189 (1965).

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Metal Ion Selectivity on the Products of a Cyclic Condensation Reaction

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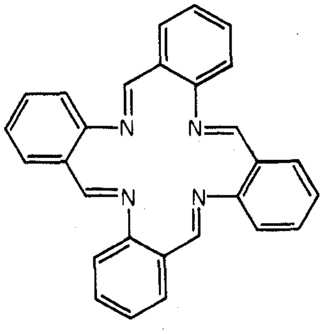
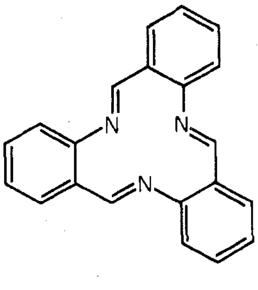
It has been demonstrated that metal ions can control the course of organic reactions by either a kinetic or a thermodynamic template effect.[1-3] The role of the specific metal ion employed in determining the nature of products must be related to electronic factors and the size of the metal ion. Presently, there have been only a few studies made on the products of a given organic reaction in which only the specific metal ion is systematically varied. One example of such a study is the self-condensation reaction of *o*-aminobenzaldehyde in the presence of various metal ions. In the presence of copper(II),[4] iron(II),[5] and cobalt(II)[5] the *o*-aminobenzaldehyde will condense forming only the coordinated tetradentate macrocyclic Schiff base tetrabenzo[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecane (TAAB) (I). However, *o*-aminobenzaldehyde in the presence of Ni(II)[6] will produce a mixture of coordinated TAAB (I) and the coordinated tridentate macrocyclic Schiff base tribenzo[*b,f,j*][1,5,9]triazacycloduodecane (TRI) (II). Cobalt(III) complexes of both TRI and TAAB have been isolated.[7,8]


I


II

At present, there is no information concerning how the size of the transition metal ion controls the degree of cyclic condensation of *o*-aminobenzaldehyde or how a transition metal ion containing less than five d electrons affects this reaction. We have begun such a study of the condensation of *o*-aminobenzaldehyde in the presence of the oxovanadium(IV) ion. There are several reasons for using the oxovanadium(IV) ion in this study. Vanadium(IV) in oxovanadium(IV) is much smaller than the ions that have been previously studied. This ion contains only one 3d electron and therefore it should function as an obvious contrast to the previously studied metal ions employed in the cyclic condensation of *o*-aminobenzaldehyde. Finally, extensive research has already been conducted on oxovanadium(IV) and oxovanadium(V)[9,10] chemistry that aided us in this research.

Experimental Section

Materials. *o*-Nitrobenzaldehyde was purchased from Matheson Coleman and Bell. *o*-Aminobenzaldehyde, 13-hydroxy-6,12-benzo-6*H*-quinazolino[3,4-*a*]quinazoline, $(oab)_3$, and the various salts $(TAAB)(HX)_2$[11] were prepared according to established procedures. Vanadyl sulfate pentahydrate was purchased from Alfa Inorganics and vanadyl dichloride was prepared by an established procedure.[12]

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer Model 337. Mass spectral data were obtained using a Varian MAT CH7 mass spectrometer. The ion source heater was approximately 240°C. All samples were solids and run using the direct-inlet system. Inlet temperature ranged from 150 to 200°C. Proton magnetic resonance spectra were recorded using a Varian Associates Model A-60. Spectra were run in deuterated acetone with TMS as an internal standard. Visible spectra were recorded using a Beckman Model DK-IIA recording spectrophotometer. Magnetic moments were determined using an Alfa Scientific Model 4600 4-in. adjustable gap electromagnet in conjunction with an Alfa Scientific Model 3002-1 current power supply. $Hg[Co(SCN)_4]$ was used as the standard and diamagnetic corrections were made using published Pascal's constants.[13] All carbon, hydrogen, and halogen and some nitrogen analyses were performed by Galbraith Microanalytical Laboratories. Most nitrogen analyses were done in this laboratory using a Coleman Model 29A nitrogen analyzer.

Syntheses. Reaction of *o*-Aminobenzaldehyde with Oxovanadium(IV) Dichloride (Compound A). Freshly prepared *o*-aminobenzaldehyde (4.7×10^{-2} mol) was dissolved in 30 ml of absolute ethanol, which had previously been degassed by bubbling oxygen-free nitrogen through it for about 0.5 hr. This mixture was then brought to reflux in a 50-ml three-necked flask which was kept under a positive pressure of nitrogen. After several minutes of refluxing, approximately 1.4×10^{-2} mol of $VOCl_2$ dissolved in 20 ml of degassed absolute ethanol was added to the reaction vessel. The reaction mixture changed from yellow to light green and after about 1 hr became a deep olive green. The reaction mixture was then refluxed for 12 hr and allowed to cool to room temperature. Upon 24 hr of standing, a green precipitate formed which was collected by centrifugation, washed several times with absolute alcohol by decantation, and then dried under vacuum for 48 hr. Anal. Calcd for $C_{25}H_{27}N_3V_4O_8Cl_2$: C, 38.95; H, 3.36; N, 5.23; Cl, 8.84. Found: C, 39.21; H, 3.57; N, 6.08; Cl, 8.97.

Reaction of $(oab)_3$ or $(TAAB)(HClO_4)_2$ with Oxovanadium(IV) Dichloride. The bisanhydro trimer $(oab)_3$ described by McGeachin[11] was allowed to react in a 3:1 molar ratio with $VOCl_2$ in absolute ethanol. The reaction mixture was refluxed for 12 hr under nitrogen and then allowed to cool to room temperature. Upon 2 days of standing, a dark green precipitate formed and was collected by centrifugation. The product was washed by decantation with absolute ethanol until the solvent remained clear. The product was then dried for several days under vacuum. The reaction of $(TAAB)(HClO_4)_2$ with $VOCl_2$ was carried out in an identical manner. (The infrared spectra of both compounds were identical with that of compound A.)

Isolation of $[(VO)_2(TRI)_2(OH)_2]Cl_4 \cdot (CH_3)_2CO$. One gram of compound A was dissolved in 1 l. of water which was strongly acidified with 20 ml of concentrated hydrochloric acid. The solution was stirred overnight, after which the color had changed from pale green to pale brown. The volume was then reduced by rotoevaporation to near dryness resulting in a dark brown viscous solution. Acetone (approximately 20 ml) was then added, followed by the addition of 100 ml of water. The solution was then rotoevaporated to 50 ml and allowed to stand several days. A dark brown precipitate formed which was collected by suction filtration in a Büchner funnel and dried overnight under vacuum. Anal. Calcd for $C_{45}H_{38}N_6O_5V_2Cl_4$: C, 54.7; H, 3.86; N, 8.52. Found: C, 54.6; H, 4.62; N, 8.36.

Isolation of $[(VO)_2(TRI)_2(OH)_2][B(C_6H_5)_4]_4$. To an aqueous solution of $[(VO)_2(TRI)_2(OH)_2]Cl_4\cdot(CH_3)_2CO$ was added a solution of sodium tetraphenylborate in water. A light brown precipitate formed immediately. The product was collected by vacuum filtration in a Büchner funnel, washed with distilled water, and dried overnight under vacuum. Anal. Calcd for $C_{136}H_{112}N_6O_4V_2B_4$: C, 80.4; H, 5.44; N, 4.13. Found: C, 81.6; H, 5.98; N, 4.27.

Isolation of $[(VO)_2(TRI)_2(OH)_2][HgI_4]_2\cdot4H_2O$. To a solution of $[(VO)_2(TRI)_2(OH)_2]Cl_4\cdot(CH_3)_2CO$ in 50:50 ethanol–water solution was added a nearly saturated solution of Na_2HgI_4. A light orange precipitate formed immediately and this was collected by vacuum filtration, washed with water, and dried under vacuum overnight. Anal. Calcd for $C_{42}H_{40}N_6O_8V_2HgI_4$: C, 22.18; H, 1.67; N, 3.69. Found: C, 22.17; H, 1.65; N, 3.41.

Discussion

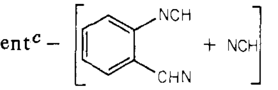
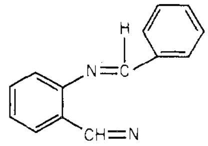
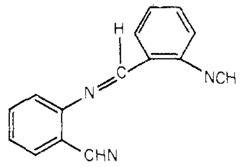
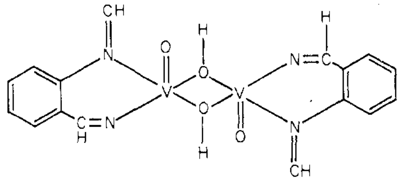
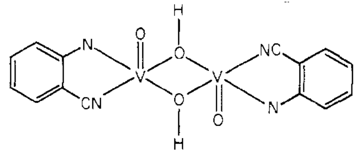
The reaction of *o*-aminobenzaldehyde with oxovanadium(IV) ion under nitrogen resulted in a deep green precipitate. The identical compound can be prepared by the reaction of vanadyl dichloride with the bisanhydro trimer of *o*-aminobenzaldehyde ($(oab)_3$) or with the salts of the tetracondensation product $(TAAB)(HClO_4)_2$ in absolute ethanol. Although the structure of this compound is not known, the mass spectral data showed two *m/e* peaks at 308 and 310 which have been assigned as $(TRI - H)^+$ and $(TRI + H)^+$.[7] Since no mass was observed at *m/e* 412, where $TAAB^+$ mass was expected,[8] it can be concluded that this precipitate contains only the TRI ligand.

The above green compound can be dissolved in aqueous HCl. After stirring of this solution overnight, acetone was added. A brown compound was isolated from the solution. The stoichiometry of this compound is $[VO(TRI)OH]Cl_2\cdot{}^1/_2(CH_3)_2CO$. Other complexes were also isolated from the reaction of $[VO(TRI)OH]Cl_2\cdot{}^1/_2(CH_3)_2CO$ and various sodium salts. These include $[VO(TRI)OH][B(C_6H_5)_4]_2$ and $[VO(TRI)OH]HgI_4\cdot2H_2O$.

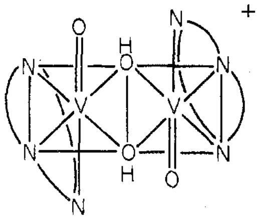
All of the above compounds are diamagnetic and show no ESR signal. Except for a weak absorption at 1425 nm for only $[VO(TRI)OH]HgI_4\cdot2H_2O$, no other bands were observed in the electronic spectra for any of the above compounds. Such data indicate that the vanadium is in the 5+ oxidation state. The infrared spectra of all of these complexes are consistent with the structure of the TRI ligand. Absorptions were observed for all of these compounds at 1610, 1490, and 1470 cm^{-1} and were assigned to the C–H ortho-disubstituted benzene.[7] There was also a strong absorption observed at 1560 cm^{-1} which has been assigned the C=N stretch. These bands in the 1610–1480-cm^{-1} range are located at similar frequencies to bands in the infrared spectra of the nickel(II) and cobalt(III) compounds containing the TRI ligand.[7] However, an additional band was observed at 1640 cm^{-1}, which was not observed for previous researchers. This band might also be due to C=N stretch. A structural trans effect has been observed in metal complexes containing the cation VO_2^+.[14] The vanadium to nitrogen bond trans to the oxo group should be weaker than the vanadium to nitrogen bond cis to the oxo group. Therefore two imine stretching frequencies are expected. A vanadium(V)–oxygen stretch was observed at 1050 cm^{-1}. Vanadium(IV)–oxygen stretches usually occur between 990 and 930 cm^{-1}.[9]

The mass spectra of all the compounds prepared in this study had *m/e* peaks at 308 and 310, which were assigned as $(TRI - H)^+$ and $(TRI + H)^+$. These same *m/e* units have been observed for $Ni(TRI)(H_2O)_3^{2+}$ and $[Co(TRI)_2]^{3+}$.[7] No peak was observed at *m/e* 412, where the $TAAB^+$ is expected. A base peak was observed at *m/e* 790 for the tetraiodomercurate derivative and is believed to be due to the parent ion of a hydroxy-bridged dimer $[VO(TRI)OH]^{2+}$ (III). (The exact numerical value of these peaks is difficult to assign because there are no other peaks between *m/e* 790 and 310 and the error in measuring is estimated to at least 5 units.) Although the base peaks were not observed for $[VO(TRI)OH]_2[B(C_6H_5)_4]_4$, its fragmentation pattern is also consistent with a dimeric structure (Table I).

Table I. Mass Spectra of $[VO(TRI)OH]_2[B(C_6H_5)_4]_4$[a]

Mass numbers[b]	Structure
732	Parent[c] − 2NCH
629	Parent[c] − 
580	Parent[c] − 
553	Parent[c] − 
428	
400	

[a] Not all *m/e* values included in the table. [b] Plus deprotonated species. [c] Parent has *m/e* 786.



III

The proton magnetic resonance spectrum of $[VO(TRI)OH]_2(HgI_4)_2\cdot4H_2O$ shows a complex multiplet between τ 2.8 and 3.4 ppm due to the aromatic protons, a doublet between τ 3.6 and 3.8 ppm due to the imine hydrogens, and a broad singlet at τ 4.3 ppm due to the hydroxo bridge protons. Integration of these absorptions indicates that the different types of protons in $[VO(TRI)OH]_2(HgI_4)_2\cdot4H_2O$ were observed in a ratio of 12:3:1.

In conclusion, the reactions of vanadyl(IV) chloride with *o*-aminobenzaldehyde, $(oab)_3$, or $(TAAB)(HClO_4)_2$ resulted in the isolation of a compound in which TRI is coordinated to vanadium(V). Even $(TAAB)(HClO_4)_2$ in the presence of vanadyl chloride will split out a C_7H_6N unit before rearranging to form a complex containing the coordinated TRI ligand. Melson and Busch[4] observed a similar selective rearrangement in the reaction of copper(II) with $(oab)_3$. Only the tetrameric condensation product $Cu(TAAB)^{2+}$ was formed. The research reported here is the only example of a metal-induced cyclic condensation reaction of *o*-aminobenzaldehyde in which only the coordinated trimeric condensation product was isolated.

This selectivity can be partially understood by comparing the size of the metal ion to the size of the hole in the macrocycle. The opening in the middle of the 16-membered TAAB ligand is too large to form strong bonds to the small vanadium(V). However, larger ions such as cobalt(II), nickel(II), and copper(II) can fit snugly inside the large TAAB ligand. On the other hand, the vanadium(V) can form a more stable compound by coordinating to the smaller 12-membered macrocycle, TRI.

Another explanation for the selectivity of TRI for VO_2^+ may be due to the cis configuration of the oxygens on VO_2^+.[14-16] These cis oxygens should make it very difficult for the cyclic tetradentate ligand TAAB to coordinate in the same plane as the vanadium(V). However, the TRI should coordinate with ease to an available face of an octahedron.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Also, support by the BGSU Faculty Research Committee is gratefully acknowledged, and we thank C. Myer for repeating some of the syntheses.

Registry No. Compound A, 56571-74-5; $[(VO)_2(TRI)_2(OH)_2]Cl_4$, 56571-75-6; $[(VO)_2(TRI)_2(OH)_2][B(C_6H_5)_4]_4$, 56488-45-0; $[(VO)_2(TRI)_2(OH)_2][HgI_4]_2$, 56488-44-9; *o*-aminobenzaldehyde, 529-23-7; $VOCl_2$, 10213-09-9; $(TAAB)(HClO_4)_2$, 56487-96-8.

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Correspondence

Comments on the Application of Symmetry Ascent Selection Rules to a Factor Group Analysis of Red Mercuric Iodide

AIC50165A

Sir:

The Raman spectrum of the red modification of mercuric iodide has been the subject of several investigations. It is therefore somewhat surprising to discover that the interpretation of its vibrational spectrum is still a subject of discussion.

In recent years it has become clear that the crystallographic point group corresponding to a particular lattice is not necessarily isomorphic to the factor group most appropriate to a vibrational analysis. Lever et al. have recently attempted to place these changes in crystallographic point group, which involve ascent to a group of higher symmetry, on a more formal basis,[1] obtaining results which are very similar to those of Boyle.[2] Hollebone and Lever[3] have applied their method of ascent in symmetry to the case of the vibrational spectrum of the red crystalline modification of HgI_2. It is the purpose of the present communication to indicate our reservations concerning the validity of their approach.

Red mercuric iodide crystallizes in the $P4_2/nmc$ space group (D_{4h}^{15}). There are two molecules in the primitive unit cell. The factor group predictions together with the commonly accepted assignments of the observed bands are given in Table I.[4-8] Of particular interest is the reason for the very low frequencies observed for the two internal E_g modes and the absence of two predicted Raman-active lattice modes.

It has been suggested[3] that these observations are understandable if the mercuric iodide lattice is regarded as a distorted cubic lattice (ca. O_h^5). However, we believe that the O_h^5 lattice cannot exist, invalidating this explanation of the spectrum.

The relationship between the lattice of face-centered cubic packed iodide ions and the red mercuric iodide structure is shown in Figure 1, where the very small departure of the iodide ion packing from ideality has been ignored. While Hollebone and Lever[3] stated that they "remove the tetragonal distortion from each sublattice", in their diagram (Figure 2 of their paper) they move only iodine atoms (moving those labeled A, A', C, C', D', F, and F' in Figure 1 of the present paper). In fact, such a movement destroys the cubic arrangement of iodide ions. Indeed, the "cubic" unit cell generated by these authors has sides of relative dimensions $1:1:2^{1/2}$!

Table I

D_{4h}^{15} modes	Obsd freq, cm^{-1}	Ref
Acoustic A_{2u}		
E_u		
Lattice B_{1g}	Not obsd	
E_g	Not obsd	
Internal A_{1g}	114	5-7
B_{1g}	142	5, 7
2 E_g	17, 29	5-7
A_{2u}	112	8
B_{2u}	Inactive	
$2E_u$	12, 26	4

Figure 1a shows a cubic close-packed arrangement of iodide ions (the unit cell being indicated) together with the corresponding lattice of mercuric ions. Figure 1b shows the unit cell of the mercuric iodide lattice; comparison with Figure 1a demonstrates the relationship between the mercuric iodide unit cell and the face-centred cubic lattice of iodide ions. This comparison is continued in Figures 1c and 1d, which show three projections of part of the structures, onto the "top" (or "bottom") and "middle" sections of the lattices shown in Figures 1a and 1b.

The question remains as to whether any simplification of the interpretation of the mercuric iodide vibrational spectrum can be obtained by a method analogous to that used by Hollebone and Lever. The only plausable displacement seems to be that of moving the mercury ions by an amount $|a/2(2^{1/2})|$ as indicated in Figure 2. This movement has the effect of placing these ions in octahedral holes and gives a unit cell (Figure 3) containing one HgI_2 molecule. All the atoms in this lattice lie on centers of symmetry and so their cartesian displacements subtend only ungerade irreducible representations of the appropriate factor group—it is isomorphic to D_{4h} (the space group is now $P4/mmm$, D_{4h}^1). Comparison with