

Because of the high temperatures, thermal analysis was employed for the remainder of the phase diagram. For this, a three section apparatus was constructed so that successive additions of metal could be made in the course of the study. The bottom section was constructed of 29 mm.  $\times$  14" fused silica with a vacuum jacket of 41 mm. fused silica on the lower two thirds. A platinum foil radiation shield was placed around the outside of the vacuum jacket. The middle segment of the apparatus consisted of a Pyrex "el," while the top, also of Pyrex, had a stopcock and two tungsten-through-glass seals for the thermocouple leads. The "el" was necessary to avoid thermal gradients across the tungsten leads. A small blower was used to cool the connecting taper joints and the stopcock. The sample itself was contained in a tantalum crucible,  $\frac{3}{4}$ " i.d.  $\times$  2", with a thermocouple well of  $\frac{5}{32}$ " tantalum tubing positioned in the center and crimped so that the tip of the thermocouple was  $\frac{1}{4}$  to  $\frac{1}{2}$ " above the bottom of the crucible. The #28 gauge chromel-alumel thermocouple was encased in an alundum shield and was equipped with small alligator clips to facilitate easy replacement.

The vacuum-jacketed portion of the apparatus was positioned in a resistance furnace, the ends of which were well packed with Fiberfrax insulation (Carborundum Co.). With power off, this apparatus had a maximum cooling rate of 7°/min. at 800°. The thermocouple potentials were recorded by a potentiometer equipped with a variable, 2-10 millivolt scale and a 0-40 millivolt zero suppression, and a Rubicon potentiometer was subsequently used to measure the recorded thermal arrests. The thermocouple in the apparatus was standardized regularly against NaCl, NaI and KCl, using the recently reported melting points<sup>34</sup>; the couple was replaced if the experimental results varied from those reported by more than one degree. No provision was made for agitating the sample during cooling other than by shaking the entire apparatus by hand.

The procedure followed in a run was to load a sample of about 25-35 millimoles of salt in the dry box and evacuate to  $10^{-6}$  mm. for about 1 hr. One-half atmosphere of dry argon was then introduced so as to keep sublimation of the trihalides to a minimum, and the sample equilibrated at the desired temperature for at least 1 hr. before a cooling curve was run. Thermal halts were reproducible to within 1° on a given sample, and unless otherwise noted, all temperatures reported are  $\pm 1^\circ$ . The entire apparatus was returned to the dry box for addition of further metal. In spite of vigorous shaking of the apparatus, supercooling was particularly bad for the neodymium iodide system at NdI<sub>1.95</sub>.

Samples for analysis were transferred in the dry box to a weighing bottle and weighed in air. After transfer of the sample, the bottle was again weighed and the necessary buoyancy correction applied. The salts were contacted with water and, after any initial reaction had subsided, sufficient 1.5 N H<sub>2</sub>SO<sub>4</sub> was added to dissolve any hydrolysis products. An acid solution was not added directly to the

subhalides as the reaction was violent enough to ignite the evolved hydrogen. With the iodides, a small amount of sodium sulfite was added to prevent air oxidation to iodine.

Where only one cation was present or where total lanthanide content was desired, the metal was titrated with EDTA using arsenazo indicator at pH 7.<sup>40</sup> Where mixed salts of two lanthanides were involved, the individual lanthanides were determined spectrophotometrically by the Analytical Service Group by the method of Banks and Klingman.<sup>41</sup> Chloride was determined gravimetrically while iodide was titrated with silver nitrate using Eosin Y as the indicator. The analyses were considered reliable if the material balance totaled  $100 \pm 0.3$  wt. %. In the results quoted, unless otherwise noted, the values of mole per cent metal are  $\pm 0.3\%$  and halide to metal ratios are  $\pm 0.01$ .

**Powder Pattern Determination.**—Samples for X-ray powder patterns were loaded in the dry box into 0.1-0.3 mm. i.d. Pyrex capillaries and sealed off. Diffraction patterns were obtained using Ni-filtered, Cu-K $\alpha$  radiation in an 11.46 cm. Debye-Scherrer camera. Values for the metals, NdCl<sub>3</sub> and NdOCl, obtained agreed very well with those reported in the ASTM file<sup>42</sup> and so are not included. Only in samples where contamination had been known to occur were a few of the stronger oxyhalide lines observed weakly; no sign of oxygen contamination was evident in regular samples.

The stronger lines and intensities for NdCl<sub>2.37</sub>, NdCl<sub>2.27</sub>, NdCl<sub>2</sub>, NdI<sub>3</sub> and NdI<sub>1.95</sub> are:

NdCl<sub>2.37</sub>: 4.11(7), 4.00(7), 3.48(4), 2.78(2), 2.71(2), 2.50 (10), 2.44(10), 2.14(4), 2.11(6), 2.09(3), 2.01(3), 1.75(3), 1.46(4), 1.43(3).

NdCl<sub>2.27</sub>: 4.01(6), 2.64(3), 2.47(10), 2.12(4), 2.10(7), 2.02(2), 1.74(3), 1.61(5), 1.60(3), 1.435(4), 1.425(5), 1.343(3).

NdCl<sub>2</sub>: 4.03(7), 3.88(7), 3.79(5), 3.57(7), 2.77(10), 2.51(6), 2.47(6), 2.38(5), 2.27(7), 2.15(5), 2.10(6), 1.96(4), 1.945(4), 1.605(3), 1.585(4).

NdI<sub>3</sub>: 6.86(8), 3.48(4), 3.28(4), 3.15(6), 2.99(10), 2.85(6), 2.57(6), 2.28(6), 2.11(8), 1.909(5), 1.808(5), 1.745(5), 1.719(5), 1.703(5), 1.686(5), 1.660(5), 1.517(6), 1.505(6), 1.337(7), 1.312(6).

NdI<sub>1.95</sub>: 4.52(3), 3.65(3), 3.51(7), 3.26(3), 3.16(8), 2.82(10), 2.81(7), 2.75(6), 2.32(3), 2.15(2), 1.986(3), 1.776(4), 1.745(3), 1.607(4), 1.513(4), 1.481(3), 1.434(3).

**Acknowledgments.**—The authors are particularly indebted to Professors F. H. Spedding and A. H. Daane for the ample supply of the pure metals, the use of the tantalum welding facilities and advice on experimental techniques.

(40) J. S. Fritz, R. T. Oliver and D. J. Pietrzyk, *Anal. Chem.*, **30**, 1111 (1958).

(41) C. V. Banks and D. W. Klingman, *Anal. Chim. Acta*, **15**, 356 (1956).

(42) X-Ray Powder Data File, P. W. Brindley, Ed., Am. Soc. for Testing Materials, Philadelphia, Pa., 1959.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS]

## Coördination Compounds Derived from Polymeric Schiff's Bases<sup>1</sup>

BY HAROLD A. GOODWIN<sup>2</sup> AND JOHN C. BAILAR, JR.

RECEIVED NOVEMBER 14, 1960

Triethylenetetramine has been condensed with 5,5'-methylene-bis-salicylaldehyde and bis-salicylaldehyde-5,5'-sulfone to obtain polymeric Schiff's bases containing recurring sexadentate units. The thermal stabilities of complexes derived from these polymers and a series of bi- and trivalent metal ions have been examined. Condensation of the above aldehydes with diethylenetriamine or 2,6-bis-(aminomethyl)-pyridine gave polymers containing five donor atoms per unit. Complexes derived from these and trivalent metal ions were prepared and were shown to exhibit greater thermal stability than the corresponding complexes derived from the sexadentate polymers.

Schiff's bases (Ia and Ib) derived from *o*-phenylenediamine and the dialdehydes, bis-salicylaldehyde-

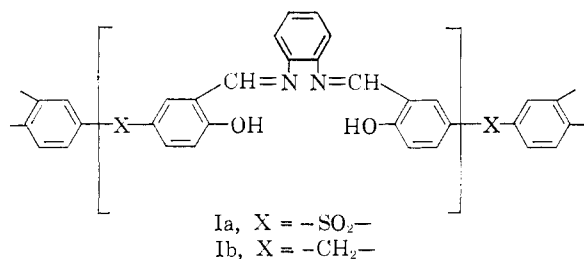
5,5'-sulfone and 5,5'-methylene-bis-salicylaldehyde, have been shown<sup>3,4</sup> to coördinate with bivalent metal ions yielding neutral coördination polymers.

(1) The work reported in this paper was done under Contract No. AF 33(616)-5486, Project No. 7340, Wright Air Development Division, Air Research and Development Command, United States Air Force.

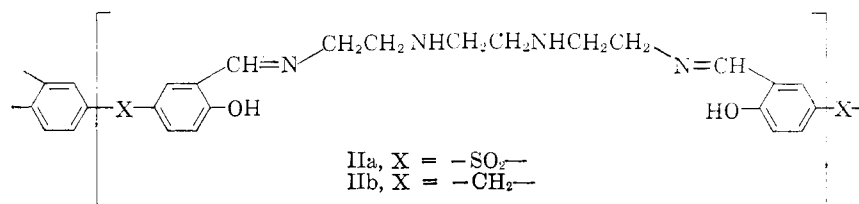
(2) Dept. of Chemistry, University of N.S.W., Broadway, N.S.W., Australia.

(3) C. S. Marvel and N. Tarköy, *J. Am. Chem. Soc.*, **79**, 6000 (1957).

(4) C. S. Marvel and N. Tarköy, *ibid.*, **80**, 832 (1958).



Condensation of the same aldehydes with triethylenetetramine yields polymeric Schiff's bases (IIa, IIb), each unit of which contains six donor atoms and is potentially capable of functioning



as a sexadentate chelating agent. The monomeric analog, bis-(salicylidene)-triethylenetetramine, has been shown<sup>5</sup> to function as a sexadentate. Its complexes with cobalt(III), iron(III) and aluminum(III) were found to be sufficiently stable to permit their resolution into optically active forms.

It was of interest to prepare complexes of IIa and IIb and to compare their thermal stabilities with those of complexes of Ia and Ib. The presence of five fused chelate rings about each metal atom would be expected to lead to increased thermal stability. Earlier work of Marvel and co-workers<sup>6</sup> indicated that complexes derived from a series of monomeric quadridentate chelating agents are, in general, more stable than complexes derived from similarly constituted sexadentates.

IIa and IIb were readily obtained as yellow, amorphous powders on condensation of triethylenetetramine with the appropriate aldehyde. Interaction of the polymeric Schiff's base with metal salts failed to yield definite coordination derivatives due, at least partly, to the low solubility of the organic polymers. More satisfactory results were obtained by slowly adding the aldehyde to a stirred solution of the metal complex of the amine. In this manner, complexes of Cu(II), Co(II), Ni(II), Fe(III), Al(III) and Cr(III) were readily obtained as highly colored, insoluble amorphous powders. The thermal stabilities of these complexes were examined using a thermogravimetric balance similar to that designed by Winslow and Matreyek.<sup>7</sup> The results are given in Table I. Co(II), Ni(II) and Cu(II) complexes of IIa show stabilities comparable to those of corresponding complexes of Ia. Thus it would not appear that the trend observed<sup>6</sup> in comparing the stabilities of complexes derived from monomeric quadridentate and sexadentate chelating agents is

necessarily followed for complexes of polymeric quadridentates and sexadentates. Fe(III), Cr(III) and Al(III) complexes of IIa are markedly less stable than the complexes derived from bivalent metals. This can be ascribed to the ionic nature of the former. Since each unit of IIa contains only two replaceable hydrogen atoms, coordination with trivalent ions must result in an excess of one positive charge per unit. Co(II), Ni(II) and Cu(II) complexes of IIb are very unstable. At 250°, decomposition to the metal oxide was virtually complete for the Co(II) and Cu(II) complexes. Their instability is similar to that observed for complexes of Ib. The greater stability of com-

plexes of IIa can be correlated with the greater acidity of the phenolic group in IIa, induced by the electron-withdrawing sulfone group.

TABLE I  
HEAT STABILITY DATA ON COMPLEXES OF IIa AND IIb<sup>a</sup>

Polymer	Metal ion	Temp., °C.	Total loss in weight, %
IIa	Cu <sup>++</sup>	250	8.0
IIa	Cu <sup>++</sup>	300	36
IIa	Ni <sup>++</sup>	250	4.0
IIa	Ni <sup>++</sup>	300	24
IIa	Co <sup>++</sup>	250	11
IIa	Co <sup>++</sup>	300	38
IIa	Fe <sup>+++</sup>	250	39
IIa	Fe <sup>+++</sup>	300	52
IIa	Cr <sup>+++</sup>	250	12
IIa	Cr <sup>+++</sup>	300	35
IIa	Al <sup>+++</sup>	250	18
IIa	Al <sup>+++</sup>	300	26
IIb	Cu <sup>++</sup>	250	81
IIb	Co <sup>++</sup>	250	56
IIb	Ni <sup>++</sup>	250	81

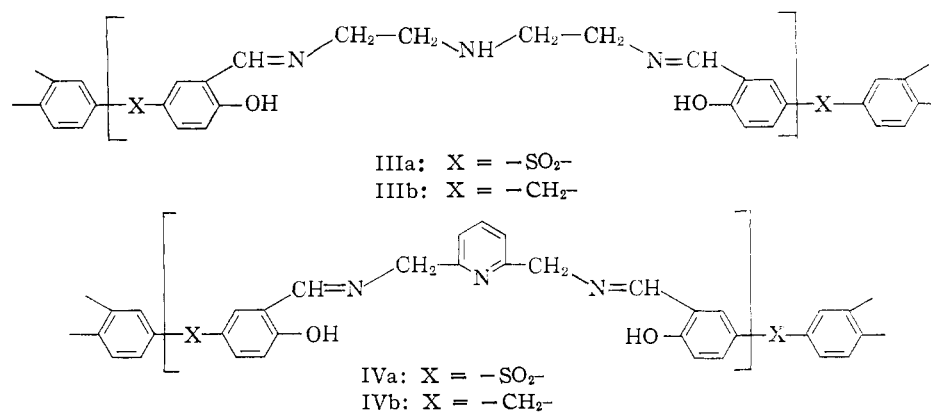
<sup>a</sup> Tests were run on approximately 200 mg. samples for a heating period of 24 hr. in an atmosphere of nitrogen. Temperature was constant within  $\pm 3^\circ$ . To eliminate any drying loss error and the hot/cold error of the balance system samples were pre-heated at 110° until their mass became constant. Each value given is the mean of two determinations. (Maximum deviation from mean 4%).

In view of the hydrolytic stability of iron(III) and aluminum (III) complexes of bis-(salicylidene)-triethylenetetramine, it was considered worthwhile to attempt to prepare complexes of trivalent metal ions with polymeric Schiff's bases related to IIa and IIb but which would lead to neutral coordination polymer units. These complexes might be expected to exhibit enhanced thermal stability over complexes of IIa with trivalent metal ions. Accordingly, diethylenetriamine was condensed with bis-salicylaldehyde-5,5'-sulfone to give the polymeric Schiff's base IIIa and 2,6-bis-(amino-methyl)-pyridine with bis-salicylaldehyde-5,5'-sulfone to give IVa. The related polymers, IIIb and IVb, were similarly prepared from the same bases

(5) B. Das Sarma and J. C. Bailar, *J. Am. Chem. Soc.*, **77**, 5476 (1955).

(6) C. S. Marvel, S. Alan Aspey and E. A. Dudley, *ibid.*, **78**, 4905 (1956).

(7) P. H. Winslow and W. Matreyek, *J. Polymer Sci.*, **22**, 315 (1956).

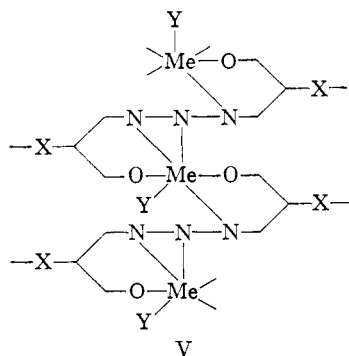


and 5,5'-methylene-bis-salicylaldehyde. Complexes derived from these polymers could not be prepared by reaction of the pre-formed Schiff's bases with the metal ion but were obtained indirectly by interaction of an appropriate metal salt or complex with the amine followed by the slow addition of the aldehyde. Fe(III), Cr(III) and Co(III) complexes were prepared. Thermal stability data for these are given in Table II.

TABLE II  
HEAT STABILITY DATA ON COMPLEXES OF IIIa, IIIb AND IVa

Polymer	Metal ion	Total % loss in weight after 24 hr. at 250°
IIIa	Co <sup>+++</sup>	9.6
IIIa	Al <sup>+++</sup>	7.8
IIIa	Cr <sup>+++</sup>	4.8
IVa	Co <sup>+++</sup>	10.0
IVa	Al <sup>+++</sup>	3.9
IVa	Cr <sup>+++</sup>	12.7
IVb	Al <sup>+++</sup>	8.0

Each unit of IIIa, IIIb, IVa or IVb contains five donor atoms potentially capable of being attached to a metal atom. In the complexes isolated, the remaining coordination position is occupied by a negative group such as chloro or nitro. Thus the complex as a whole is neutral. The manner in which these Schiff's bases function as chelating



agents is not definitely known. Their function as quinquedentates about a single metal atom would appear to induce almost insuperable steric strain in the resulting coordination compound due to the spatial demands of the bonds from the azomethine nitrogen atoms. Coordination through all five donor atoms but to two separate metal atoms (see V) would overcome this strain and such a structure

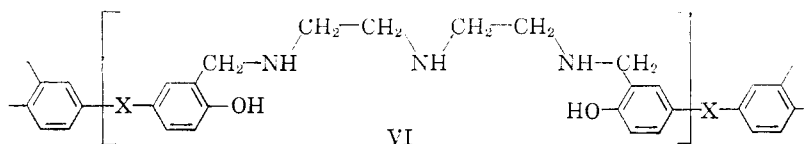
would account equally well for the analytical values obtained for the complexes. Such a formulation necessitates extensive cross-linking of the polymer chains. Further information on the function of these Schiff's bases as chelating agents probably would be best obtained by a study of the monomeric analogs. The complexes obtained are very insoluble in the common solvents so that it is not possible to determine their molecular weights. The physical appearance of the complexes would suggest that their molecular weights are not high (probably not greater than 10,000).

The data in Table II indicate a significant increase in stability for complexes in which the ionic charge of the metal ion is satisfied by the donor groups. This effect is most pronounced with the aluminum complex of IVa.

When IIIb was allowed to react with hexamine cobalt(III) nitrate, a polymer was obtained in which five of the six coordination positions of each cobalt were occupied by atoms in the polymer chain and the sixth by a molecule of ammonia. In this case, the ionic charge on the metal is not fully satisfied by groups coordinated to it, and qualitative tests indicated a lower thermal stability.

Reduction of the azo-methine groups in IIIa, IIIb, IVa or IVb would lead to considerably increased flexibility in the molecules and the reduced compounds would be expected to coordinate, as quinquedentates, to octahedral metal ions with less strain. It was hoped that complexes derived from the reduced Schiff's bases would exhibit increased thermal stability. VI was obtained on catalytic hydrogenation of IIIb in glacial acetic acid as a hygroscopic, brittle, resinous solid, which was not analytically pure. Analysis suggested that solvent molecules were retained in it.

Reaction of VI with trichloro-tris-(pyridine)-chromium(III) in dimethylformamide solution ultimately led to the formation of a deep violet complex in which one chloro group remained coordinated to the chromium, the remaining five octahedral positions being occupied by a unit of VI. As can be seen from Table III, this complex is considerably less resistant to heat than the chromium complex of the unreduced Schiff's base (IIIa). A similar trend was observed in comparing the thermal stabilities of the zinc complexes of bis-(salicylidene)-ethylenediamine (VII) and 1,6-bis-(*o*-hydroxyphenyl)-2,4-di-*az*a-hexane(VIII)



(see Table III). Thus, it would not be profitable to study other complexes of molecules related to VI, with the intention of obtaining thermally stable compounds.

TABLE III  
HEAT STABILITY DATA ON COMPLEXES OF REDUCED SCHIFF'S BASES

Ligand	Metal ion	Temp., °C.	Total % loss in weight after 24 hr.
IIIb	Cr <sup>+++</sup>	250	15
VI	Cr <sup>+++</sup>	250	28
VII	Zn <sup>++</sup>	300	9.5
VIII	Zn <sup>++</sup>	300	28

TABLE IV  
ANALYTICAL DATA FOR POLYMERIC SCHIFF'S BASES

Compound	Formula	Carbon		Hydrogen	
		Calcd.	Found	Calcd.	Found
IIa	(C <sub>20</sub> H <sub>24</sub> N <sub>4</sub> O <sub>4</sub> S) <sub>n</sub>	57.7	56.7	5.8	5.3
IIb	(C <sub>21</sub> H <sub>26</sub> N <sub>4</sub> O <sub>2</sub> ) <sub>n</sub>	68.9	70.2	7.2	7.0
IIIa	(C <sub>18</sub> H <sub>19</sub> N <sub>3</sub> O <sub>4</sub> S) <sub>n</sub>	57.9	56.7	5.1	5.1
IIIb	(C <sub>19</sub> H <sub>21</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>n</sub>	70.7	70.7	6.6	6.4
IVa	(C <sub>21</sub> H <sub>17</sub> N <sub>3</sub> O <sub>4</sub> S) <sub>n</sub>	61.9	59.9	4.2	5.0
IVb	(C <sub>22</sub> H <sub>19</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>n</sub>	73.9	71.5	5.4	5.5

TABLE V

Schiff's base	Metal ion	Color	Formula	Carbon		Hydrogen	
				Calcd.	Found	Calcd.	Found
IIa	Co <sup>++</sup>	Light brown	(C <sub>20</sub> H <sub>22</sub> N <sub>4</sub> O <sub>4</sub> SCO·1/2H <sub>2</sub> O) <sub>n</sub>	49.8	49.7	4.8	4.9
IIa	Ni <sup>++</sup>	Light brown	(C <sub>20</sub> H <sub>22</sub> N <sub>4</sub> O <sub>4</sub> SNi·1/2H <sub>2</sub> O) <sub>n</sub>	49.8	49.4	4.8	5.2
IIa	Cu <sup>++</sup>	Brown-green	(C <sub>20</sub> H <sub>22</sub> N <sub>4</sub> O <sub>4</sub> S·Cu) <sub>n</sub>	50.2	50.8	4.7	5.4
IIa	Fe <sup>+++</sup>	Dark brown	(C <sub>20</sub> H <sub>22</sub> N <sub>4</sub> O <sub>4</sub> SFeNO <sub>3</sub> ) <sub>n</sub>	45.2	45.5	4.2	5.1
IIa	Cr <sup>+++</sup>	Light brown	(C <sub>20</sub> H <sub>22</sub> N <sub>4</sub> O <sub>4</sub> SCrCl·1.5H <sub>2</sub> O) <sub>n</sub>	45.4	45.0	4.8	5.7
IIa	Al <sup>+++</sup>	Yellow-brown	(C <sub>20</sub> H <sub>22</sub> N <sub>4</sub> O <sub>4</sub> SAINO <sub>3</sub> ·3H <sub>2</sub> O) <sub>n</sub>	43.2	43.1	5.1	4.8
IIb	Cu <sup>++</sup>	Brown-green	(C <sub>21</sub> H <sub>24</sub> N <sub>4</sub> O <sub>2</sub> Cu) <sub>n</sub>	58.8	59.2	5.7	5.5
IIb	Ni <sup>++</sup>	Dark brown	(C <sub>21</sub> H <sub>24</sub> N <sub>4</sub> O <sub>2</sub> Ni) <sub>n</sub>	59.6	58.9	5.7	5.5
IIb	Co <sup>++</sup>	Dark brown	(C <sub>21</sub> H <sub>24</sub> N <sub>4</sub> O <sub>2</sub> Co) <sub>n</sub>	59.6	58.9	5.7	5.3
IIIa	Co <sup>+++</sup>	Brown	(C <sub>18</sub> H <sub>17</sub> N <sub>4</sub> O <sub>6</sub> SCO) <sub>n</sub>	45.7	46.5	3.6	3.8
IIIa	Al <sup>+++</sup>	Yellow	(C <sub>18</sub> H <sub>17</sub> N <sub>3</sub> O <sub>4</sub> SAICl·3H <sub>2</sub> O) <sub>n</sub>	44.3	43.8	4.8	5.3
IIIa	Cr <sup>+++</sup>	Brown	(C <sub>18</sub> H <sub>17</sub> N <sub>3</sub> O <sub>4</sub> SCrCl·3H <sub>2</sub> O) <sub>n</sub>	42.2	41.6	4.5	5.2
IIIb	Al <sup>+++</sup>	Yellow	(C <sub>19</sub> H <sub>19</sub> N <sub>3</sub> O <sub>2</sub> AlCl·2H <sub>2</sub> O) <sub>n</sub>	54.3	54.3	5.5	5.8
IIIb	Cr <sup>+++</sup>	Brown	(C <sub>19</sub> H <sub>19</sub> N <sub>3</sub> O <sub>2</sub> CrCl·H <sub>2</sub> O) <sub>n</sub>	53.4	53.2	5.0	5.4
IIIb	Co <sup>+++</sup>	Brown	(C <sub>19</sub> H <sub>22</sub> N <sub>6</sub> O <sub>5</sub> Co) <sub>n</sub> <sup>a</sup>	48.6	43.9	4.7	4.6
IVa	Co <sup>+++</sup>	Dark brown	(C <sub>21</sub> H <sub>16</sub> N <sub>4</sub> O <sub>6</sub> SCO·3H <sub>2</sub> O) <sub>n</sub>	44.7	46.4	3.8	4.2
IVa	Al <sup>+++</sup>	Pale brown	(C <sub>21</sub> H <sub>16</sub> N <sub>3</sub> SO <sub>4</sub> AlCl·3H <sub>2</sub> O) <sub>n</sub>	48.3	48.3	4.1	4.6
IVa	Cr <sup>+++</sup>	Brown	(C <sub>21</sub> H <sub>16</sub> N <sub>3</sub> SO <sub>4</sub> CrCl) <sub>n</sub>	51.1	51.1	3.1	3.1
IVb	Al <sup>+++</sup>	Light brown	(C <sub>22</sub> H <sub>17</sub> N <sub>3</sub> O <sub>2</sub> AlCl·4H <sub>2</sub> O) <sub>n</sub>	53.9	53.8	5.2	5.5

<sup>a</sup> Calcd. for N, 14.9. Found, 12.8.

### Experimental

*o*-Cresol was converted to 3,3'-dimethyl-4,4'-dihydroxydiphenylsulfone by the method of Chataway and Bell,<sup>8</sup> and this was oxidized with chromic acid to bis-salicylaldehyde-5,5'-sulfone according to the method of Marvel and Tarköy.<sup>4</sup> 5,5'-Methylene-bis-salicylaldehyde was obtained on treating salicylaldehyde with trioxane.<sup>3</sup> 2,6-Bis-(aminomethyl)pyridine was prepared by reduction of pyridine-2,6-di-aldoxime as described by Lions and Martin.<sup>9</sup> Commercial diethylenetriamine and triethylenetetramine were redistilled *in vacuo* before use.

(8) F. D. Chattaway and A. E. Bell, *J. Chem. Soc.*, 43 (1934).

(9) F. Lions and K. V. Martin, *J. Am. Chem. Soc.*, **79**, 2733 (1957).

**Preparation of Polymeric Schiff's Bases.**—The polymeric Schiff's bases IIa, IIb, IIIa, IIIb, IVa and IVb were all prepared from the appropriate amine and aldehyde according to the method given below for the preparation of IIa. Analytical data are listed in Table IV.

**Polymeric Schiff's Base from Bis-salicylaldehyde-5,5'-sulfone and Triethylenetetramine.**—To a hot, vigorously stirred solution of triethylenetetramine (0.15 g.) in absolute ethanol (250 ml.) bis-salicylaldehyde 5,5'-sulfone (0.306 g.) in hot ethanol (150 ml.) was slowly added over a period of 45 minutes. A bright yellow solution was obtained. After about 30 minutes the solution became cloudy and a yellow amorphous powder separated. This was collected on cooling, washed with ethanol, and dried *in vacuo*. It did not melt below 280° but slowly decomposed above 220°.

**Preparation of Complexes of Polymeric Schiff's Bases.**—Complexes of the various Schiff's bases were all prepared by the general method outlined below. Cobalt(II), nickel(II) and copper(II) complexes were prepared from the appropriate metal acetates. Cobalt(III) complexes were prepared from trinitro-triammine-cobalt(III),<sup>10</sup> chromium(III) complexes were prepared from trichloro-tris-(pyridine)-chromium(III),<sup>11</sup> iron(III) and aluminum(III) complexes were prepared from the nitrate and chloride, respectively (the aluminum complex of IIa was prepared from aluminum nitrate). The cobalt (III) complex of IIIb was prepared from hexammine cobalt (III) nitrate. The period of reaction varied in some instances but this was generally determined by the time taken for complete precipitation of the product. The analytical data are given in Table V.

To a hot, stirred solution of amine (1 mmole) in dimethylformamide (50 ml.) containing the appropriate metal salt or complex (1 mmole), a solution of aldehyde (1 mmole) in dimethylformamide (30 ml.) was slowly added. The mixture was stirred and gently refluxed for several hours. Generally after about 30 minutes a dark precipitate of the polymeric complex separated. This was washed with dimethylformamide and ethanol and dried *in vacuo*. In many instances the complexes were found to be hygroscopic and to contain water of solvation.

(10) W. G. Palmer "Experimental Inorganic Chemistry," Cambridge University Press, 1954, p. 539.

(11) P. Pfeiffer, *Z. anorg. Chem.*, **24**, 283 (1900); J. C. Taft and M. M. Jones, *J. Am. Chem. Soc.*, **82**, 4196 (1960).

1,6-Bis-(*o*-hydroxyphenyl)-2,4-di-aza-hexane-zinc(II).—Zinc dust (30 g.) and acetic acid (100 ml.) were added to a hot, vigorously stirred solution of ethylenediamine (6 g.) in 95% ethanol (300 ml.). A solution of salicylaldehyde (24 g.) in ethanol (150 ml.) was slowly added over a period of 90 minutes. Zinc dust (70 g.) and acetic acid (200 ml.) were added in small amounts at intervals over a period of 3 hr. and the mixture allowed to stand overnight. The zinc acetate and unchanged zinc were filtered and the excess alcohol and acetic acid removed by distillation under reduced pressure. The residual syrup was dissolved in water and on adding excess sodium hydroxide solution a pale cream precipitate of the zinc complex of VIII separated. This was obtained pure on recrystallization from aqueous dimethylformamide solution.

*Anal.* Calcd. for  $[C_{16}H_{18}N_2O_2Zn]$ : C, 57.3; H, 5.4; Zn, 19.4. Found: C, 57.2; H, 5.5; Zn, 19.6.

Reduction of the Polymeric Schiff Base from Diethylene-triamine and 5,5'-Methylene-bis-salicylaldehyde.—5,5'-Methylene-bis-salicylaldehyde (5.12 g.) in hot glacial acetic acid (100 ml.) was added to a hot, stirred solution of diethylenetriamine (2.06 g.) in glacial acetic acid (50 ml.). Heat was generated and the solution became brown. It was stirred and gently heated for 75 minutes. After cooling, the solution was subjected to hydrogenation, using platinum dioxide as catalyst and a pressure of 1,000 p.s.i. for 24 hr. After this time the acetic acid was removed by distillation under

reduced pressure. The dark brown, syrupy residue was diluted with water and distillation repeated three more times to remove as much of the acetic acid as possible. Finally the residue was dissolved in ethanol. This solution was filtered and the filtrate evaporated by distillation at atmospheric pressure. When as much of the ethanol as possible had been removed in this manner the residual syrup was dried *in vacuo*. It rapidly foamed and ultimately became brittle and resinous. The material is very hygroscopic and was stored *in vacuo*.

*Anal.* Calcd. for  $(C_{19}H_{25}N_3O_2)_n$ : C, 69.7; 7.7; N, 12.8. Calcd. for  $(C_{19}H_{25}N_3O_2 \cdot 2CH_3COOH \cdot C_2H_5OH)_n$ : C, 60.7; H, 8.0; N, 8.5. Found: C, 60.3; H, 8.0; N, 8.2.

Coördination of Reduced Schiff's Base Polymer with Chromium.—A suspension of trichloro-tris-(pyridine)-chromium(III) (0.79 g.) in dimethylformamide (20 ml.) was added to a warm, stirred solution of the above polymer (0.66 g.) in dimethylformamide (20 ml.). Soon after mixing, the  $[Crpy_3Cl_3]$  dissolved and a light violet solution was obtained. The mixture was stirred and gently refluxed for three days. The solution slowly became blue and a dark violet, almost black, amorphous precipitate gradually separated. This was washed with dimethylformamide and ethanol and dried *in vacuo*.

*Anal.* Calcd. for  $(CrCl_3 \cdot H_{23}N_3O_2Cl \cdot 1.5H_2O)_n$ : C, 51.8; H, 6.0; N, 9.6. Found: C, 51.9; H, 6.0; N, 9.9.

[CONTRIBUTION NO. 640 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE]

## Chemistry of Boranes. I. Reactions of Boron Hydrides with Metal and Amine Salts

BY V. D. AFTANDILIAN, H. C. MILLER AND E. L. MUEBERTIES

RECEIVED SEPTEMBER 16, 1960

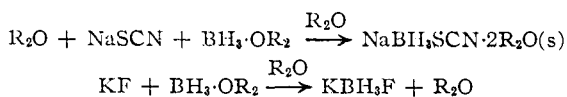
Diborane, tetraborane and decaborane react readily with certain metal salts, *e.g.*, NaCN, to form substituted borohydride salts ( $NaH_2BCNBH_3$ ,  $NaB_4H_7CN$  and  $NaB_{10}H_{12}CN$ ) which are generally isolated as etherates. Ammonium and amine salts with diborane initially form substituted borohydrides, but at 0–25° hydrogen loss is spontaneous and the final product is an ammonia or amine adduct of a substituted borane



### Introduction

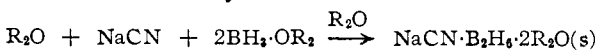
The behavior of boron hydrides as electrophilic reagents is well characterized.<sup>1</sup> One class reaction within this chemistry is complex formation with  $H^-$  to form borohydride anions; however, apparently few other anions have been investigated with the boranes.<sup>1</sup> We have found that a variety of inorganic and organic anions react with boranes to form substituted borohydride anions.

**Diborane.**—Borane ( $BH_3$ ) in the form of an ether complex reacts with metal thiocyanates and fluorides



The  $B^{11}$  spectrum of  $BH_3SCN^-$  (or  $BH_3NCS^-$ ) consists of a quadruplet which is consistent with a monosubstituted borohydride anion structure. Hydrolytic stability of  $BH_3F^-$  is poor in neutral solution whereas that of the thiocyanate derivative appears to be comparable to  $BH_4^-$ .

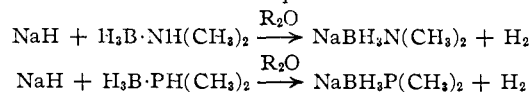
Sodium cyanide and diborane do not follow the above stoichiometry but react as



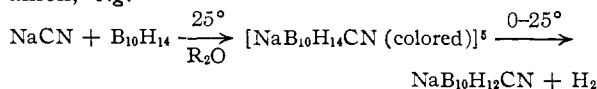
(1) For review see F. G. A. Stone, *Quart. Rev. (London)*, **9**, 174 (1955); D. T. Hurd, "Chemistry of the Hydrides," John Wiley and Sons, Inc., New York, N. Y., 1952; "Gmelins Handbuch der Anorg. Chemie," BOR **13**, Verlag Chemie, GMBH, Weinheim, 1954; R. W. Parry and L. J. Edwards, *J. Am. Chem. Soc.*, **81**, 3554 (1959).

The  $B^{11}$  spectrum of this product consists of two quadruplets of equal intensity, and the only reasonable structure consistent with this is  $(H_3BCNBH_3)^-$ .<sup>2</sup> Hydrolytic stability of this salt is comparable to  $NaBH_4$ . Sodium cyanide and tetraborane also form  $NaH_3BCNBH_3$  plus a second product believed to be  $NaB_3H_7CN$ .<sup>3</sup> Pentaborane is apparently not cleaved by cyanide ion and a simple salt,  $NaB_5H_9CN$ , is obtained.

Another new, simple route to substituted borohydride etherates is the protolysis of sodium hydride and borane-base complexes



**Decaborane.**—We have found a characteristic reaction of decaborane with metal salts and ammonium salts in which the anion displaces a mole of hydrogen from decaborane to give a  $B_{10}H_{12}X^-$  anion,<sup>4</sup> *e.g.*



(2) One quadruplet was slightly broadened. This probably represents the boron atom bonded to a nitrogen atom since the latter nucleus has a quadrupole moment that would affect the relaxation time.

(3) It has been established that tetraborane can be cleaved symmetrically to effectively yield  $BH_3$  and  $B_3H_7$  fragments. *Cf.* R. W. Parry and L. J. Edwards, *J. Am. Chem. Soc.*, **81**, 3554 (1959).

(4) Decaborane and  $H^-$  form  $B_{10}H_{12}^-$ . *Cf.* W. V. Hough and L. J. Edwards, paper presented before the Division of Inorganic