

The bathochromic shift observed in the case of 2,5-dicarbethoxy-3,4-dihydroxycyclopentadiene-2,4 (VI) in going from alcoholic hydrogen chloride as solvent to concentrated sulfuric acid contrasts with the hypsochromic shift in the case of the sulfone (III) under the same conditions (Figs. 1, 3, 4), and is interpreted as involving conjugate acid formation at a carbethoxyl group in VI with consequent elimination of charge separation in the resonating chromophoric system.

### Summary

A study of the acidic strengths and ultraviolet absorption spectra of certain dihydroxythiophene-1-oxides and 1-dioxides has provided further evidence for an expanded valence shell for the sulfur atom in the sulfone configuration.

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## Inorganic Complex Compounds Containing Polydentate Groups. II. The Complexes Formed between Triethylenetetramine and the Nickel(II) Ion

BY HANS B. JONASSEN AND B. E. DOUGLAS<sup>1,2,3</sup>

The stereochemical configuration of the quadricovalent complexes of the nickel(II) ion has been extensively investigated. This ion has been shown to be able to direct its valence bonds toward the corners of a tetrahedron<sup>4,5,6,7</sup> and of a plane.<sup>6,7,8,9</sup>

Various criteria have been used to obtain information about the configuration of these complex compounds. Lifschitz and co-workers<sup>10</sup> attempted to relate color and magnetic properties to bond direction. Yellow compounds were classed as planar because of diamagnetism; blue paramagnetic compounds indicated tetrahedral bond direction. This distinguishing characteristic, however, breaks down in many cases.

Mellor and co-workers<sup>7</sup> found that the electro-negativity of the coordinating group influences the stereochemical configuration. The very electro-negative donor atom, oxygen, imposes tetrahedral  $sp^3$  bonds upon the nickel(II) ion. As the electro-negativity decreases through nitrogen to sulfur, the bonds are directed toward the corners of a coplanar square. In the compounds containing four nitrogen donor atoms the statistical distribution is about half planar, half tetrahedral. Many complexes of this type can show both configurations.<sup>10</sup> Other factors such as steric hindrance due to coordinating groups and functional groups attached to donor atom also affect the configuration of these complexes.

In most of these complexes the coordinating group is a mono- or bidentate group. Very few quadridentate complexes containing the same donor atom have been investigated. In all of these cases<sup>8,9,11</sup> the configuration of the coordinating group imposes a planar configuration upon the complex.

This study was undertaken to determine the type of configuration of the complex or complexes formed between the nickel(II) ion and triethylenetetramine ( $NH_2C_2H_4NHC_2H_4NHC_2H_4NH_2$ ) (abbreviated trien). This quadridentate base can orient itself with little difference in strain around a metal ion exhibiting tetrahedral or planar valence bond direction.

Since the configuration of the trien molecule does not impose a definite bond direction upon the central ion, this investigation may throw more light upon the factors which influence the direction of valence forces in the complexes containing the nickel(II) ion.

Since the nickel(II) ion also has a tendency to form octahedral complexes, the data obtained in this study may also indicate the ease of conversion of nickel(II) complex ions from tetra- to hexacoordination. This may lead to some information about the configuration of the tetracoordinated complexes since Dwyer and Mellor<sup>12</sup> found that planar diamagnetic nickel(II) complex ions show little tendency to assume sixfold coordination. Paramagnetic tetrahedral complex compounds, however, can easily be converted to an octahedral configuration by the uptake of two more donor groups.

### Experimental

**A. Spectrophotometric Studies. 1. Absorption Data.**—Standard solutions of 0.05 *M* nickel chloride and 0.05 *M* trien were used in the absorption studies. Fixed amounts of nickel chloride were mixed with varying amounts of trien to give solutions with the following ratios

(11) P. Ray and H. Ray, *J. Indian Chem. Soc.*, **21**, 163 (1944).

(12) E. P. Dwyer and D. P. Mellor, *THIS JOURNAL*, **63**, 81 (1941).

(1) Based upon the M.S. thesis of B. E. Douglas, Tulane University, 1947.

(2) Presented in part before Division of Physical and Inorganic Chemistry at the 112th American Chemical Society Meeting, New York, September, 1947.

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(4) L. O. Brockway and P. L. Cross, *J. Phys. Chem.*, **13**, 828 (1935).

(5) W. Klemm and K. H. Raddatz, *Z. anorg. allgem. Chem.*, **250**, 204 (1942).

(6) I. Lifschitz and K. M. Dijkema, *Rec. trav. chim.*, **60**, 581 (1941).

(7) D. P. Mellor and J. Craig, *J. Proc. Royal Soc. New South Wales*, **74**, 475 (1941).

(8) G. T. Morgan and F. N. Burstall, *J. Chem. Soc.*, 1672 (1938).

(9) I. Woodward, *J. Chem. Soc.*, 601 (1940).

(10) I. Lifschitz, J. G. Bos and K. M. Dijkema, *Z. anorg. allgem. Chem.*, **242**, 97 (1939).

of nickel chloride to trien: 1:2, 2:1, 3:2, 1:1, 2:3, 1:2, 1:4. A drop of hydrochloric acid was added to each of the first three solutions to prevent hydrolysis of the non-complexed nickel(II) ion. The optical density values of the solutions were determined between the wave lengths of 500 and 1000  $m\mu$  using a Beckman spectrophotometer and matched Corex cells with a depth of 1 cm. The optical density curves are shown in Fig. 1. No change in absorption characteristics was obtained after the ratio of nickel(II) to trien becomes smaller than 2:3. The optical density values for the 1:2 and 1:4 nickel(II) ion to trien solutions are therefore not shown.

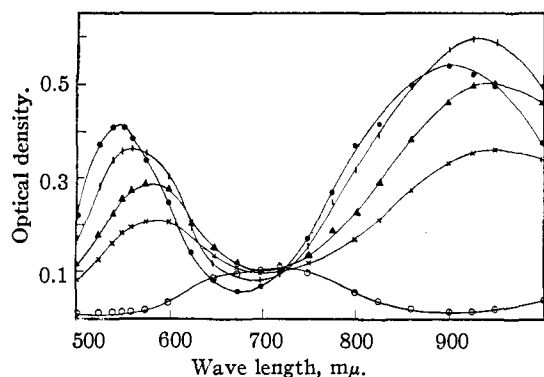


Fig. 1.—Absorption curves for solutions containing 0.05  $M$  of nickel chloride and 0.0 to 0.075  $M$  of trien: —○—, 0.05  $M$  nickel chloride; —×—, ratio of 2:1 ( $Ni^{2+}$ :trien); —▲—, ratio of 3:2 ( $Ni^{2+}$ :trien); —□—, ratio of 1:1 ( $Ni^{2+}$ :trien); —●—, ratio of 2:3 ( $Ni^{2+}$ :trien).

**Discussion.**—As Fig. 1 shows the absorption characteristics of solutions containing a mole ratio of nickel(II) ion to trien of 2:1, 3:2 and 1:1 are very similar indicating the existence of a 1:1 complex  $[Ni\ trien]^{+2}$  ion in the solution. However, after the 1:1 ratio has been exceeded a shift of the absorption maximum towards shorter wave lengths occurs indicating the existence of another colored complex in solution. Since no further change occurs after the ratio becomes smaller than 2:3, the composition of the other complex should correspond to  $[Ni_2\ trien_3]^{+4}$  and no other colored complex with a mole ratio smaller than 2:3 should be present in the solution.

**2. Continuous Variation Studies.**—Solutions 0.1  $M$  in nickel chloride and 0.1  $M$  in trien were prepared for the continuous variation studies.<sup>18</sup> The optical density of solutions whose total solute concentration was 0.1  $M$  with varying amounts of nickel(II) ions and trien was measured at the wave lengths 550, 565, 580, 600 and 860  $m\mu$ . In Fig. 2  $x$  (the fraction of trien) is plotted against  $y$  (the difference between the observed optical density of the complex and the optical density calculated for no reaction) for the wave lengths 580 and 860  $m\mu$ . Figure 3 shows a similar plot for the

nickel chloride–trien system at 550  $m\mu$ . In this graph, however,  $y'$  ( $y'$  is the difference between the observed optical density and that calculated for the 1:1 complex) is plotted against  $x$  (fraction of trien).

**Discussion.**—The continuous variation studies indicate that, in solutions containing nickel(II) ions and trien, the  $[Ni\ trien]^{+2}$  ion is present as is shown by the maxima at  $x = 0.5$  in Fig. 2.

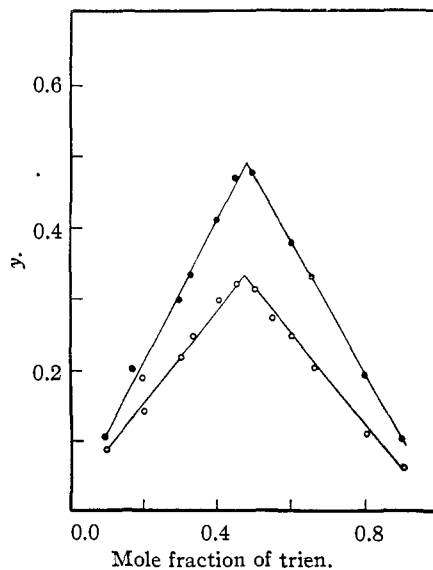


Fig. 2.—Continuous variation studies  $Ni^{2+}$ -trien system: ●, 860  $m\mu$ ; ○, 580  $m\mu$ .

Figure 3 shows a maximum at  $x = 0.6$  indicating the existence of the  $[Ni_2\ trien_3]^{+4}$  ion. No other maxima are obtained in these studies substantiating the conclusions drawn from the absorption

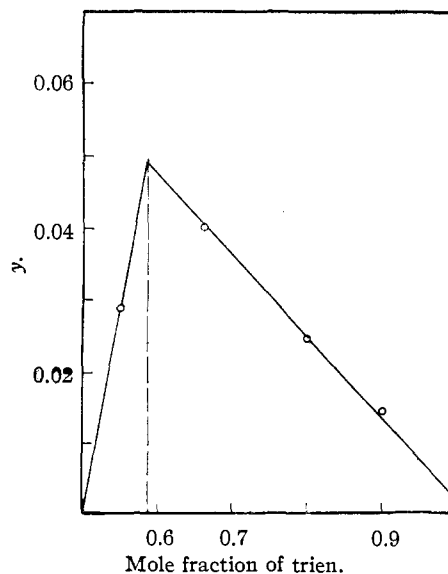


Fig. 3.—Continuous variation studies  $Ni^{2+}$ -trien system: ○, 550  $m\mu$ .

(18) W. C. Vosburgh and G. R. Cooper, *THIS JOURNAL*, **63**, 437 (1941).

data about the absence of colored complex ions of lower mole ratio in these solutions.

## B. Preparation of Complex Compounds

1. **Special Reagents.**—The trien was a Technical Grade of 79% purity purchased from Eastman Kodak Company, Rochester, New York. The trien used in the absorption studies was distilled over sodium at reduced pressure (the fraction collected boiled at 139–141° at 10 mm. pressure) and was standardized potentiometrically.<sup>14</sup> All other chemicals used were standard reagents of C. P. quality.

2. **Preparation of the Nickel(II) Chloride Complex**  $[\text{Ni}_2 \text{trien}_3] \text{Cl}_4 \cdot 2\text{H}_2\text{O}$ .—Twenty ml. of a 2 molar solution of trien was added to 10 ml. of 2 molar nickelous chloride with stirring. The color of the solution changed from green to a deep purple. This solution was evaporated almost to dryness, whereupon a mixture of 20 ml. of methyl alcohol and 10 ml. of ether was added. A light pink precipitate settled out immediately. It was washed with 20 ml. of methyl alcohol and 20 ml. of ether and dried in the oven at 65°.

*Anal.* Calcd. for  $[\text{Ni}_2 \text{trien}_3] \text{Cl}_4 \cdot 2\text{H}_2\text{O}$ : Cl, 19.14; Ni, 15.5; C, 29.2; H, 7.9; N, 22.9. Found: Cl, 19.2; Ni, 15.7; C, 29.3; H, 7.7; N, 23.0.

3. **Preparation of the Nickel(II) Nitrate Complex.**—The complex nitrate was prepared in the same manner as the chloride. The precipitate obtained is slightly more violet in color.

*Anal.* Calcd. for  $[\text{Ni}_2 \text{trien}_3] (\text{NO}_3)_4 \cdot \text{H}_2\text{O}$ : Ni, 13.8; C, 26.3; H, 6.6; N, 20.4. Found: Ni, 13.9; C, 26.2; H, 6.7; N, 20.3.

4. **Preparation of the Nickel(II) Tetrachloroplatinite Complex**  $[\text{Ni}_2 \text{trien}_3] [\text{PtCl}_4]_2$ .—One hundred ml. of 0.01 *M* nickel chloride and 200 ml. of 0.005 *M* trien in aqueous solution were mixed in a beaker. A color change from green to blue to purple occurred. To this purple solution was added slowly and with stirring 100 ml. of 0.01 *M* potassium chloroplatinite. A light pink precipitate settled out of the solution immediately. The precipitate was washed successively with 200-ml. portions of cold water, 95% alcohol and ether. Drying to constant weight led to the formation of a light green precipitate which decomposed at 250–260°.

*Anal.* Calcd. for  $[\text{Ni}_2 \text{trien}_3] (\text{PtCl}_4)_2$ : Pt, 30.8; Ni, 9.30; C, 17.1; H, 4.3. Found: Pt, 30.8; Ni, 9.40; C, 16.8; H, 4.2. The loss of weight was found to be 2.66% which corresponds to two molecules of water of hydration in the pink complex compound.

**Discussion.**—The compounds obtained from the solutions containing nickel(II) ion, chloride or nitrate ions, and trien show a coordination number of 6 with octahedral valence bond distribution.

Since the spectrophotometric investigation of solutions containing nickel(II) ions and trien also indicates the existence of the  $[\text{Ni} \text{trien}]^{+2}$  ion, potassium chloroplatinite was added. It was hoped that the large chloroplatinite ion would form a precipitate with the 1:1 complex ion similar to the insoluble  $[\text{Pt} \text{trien}] [\text{Pt} \text{Cl}_4]$ .<sup>15</sup> However, the  $[\text{Ni}_2 \text{trien}_3] [\text{Pt} \text{Cl}_4]_2$  precipitated under these conditions indicating that even though the tetra-coordinated  $[\text{Ni} \text{trien}]^{+2}$  ion is present in solution its chloroplatinite is more soluble than that of the  $[\text{Ni}_2 \text{trien}_3]^{+4}$  ion.

(14) H. B. Jonassen, R. B. LeBlanc and R. Rogan, *THIS JOURNAL*, in press.

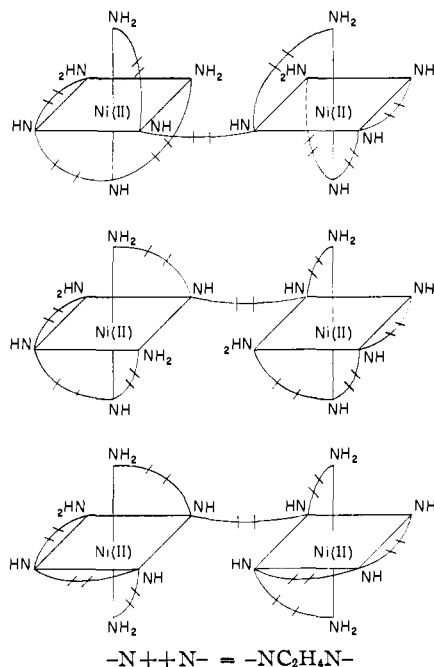
(15) N. L. Cull and H. B. Jonassen, *ibid.*, **71**, 4097 (1949).

C. **Attempted Resolution of  $[\text{Ni}_2 \text{trien}_3] \text{Cl}_4$ .**—To 4 g. of  $[\text{Ni}_2 \text{trien}_3] \text{Cl}_4$  dissolved in 45 g. of water was added 15 g. of ammonium *d*- $\alpha$ -bromocamphor- $\pi$ -sulfonate. Upon cooling in ice-water and allowing air to blow over the solution, some of the excess resolving agent crystallized out. Further evaporation of the solution of the complex *d*- $\alpha$ -bromocamphor- $\pi$ -sulfonate produced several fractions. These fractions showed the same rotation and no measurable difference in physical properties. Similar results were obtained with ammonium *d*-tartrate.

**Discussion.**—Since it was not possible to resolve the complex ion, three possible explanations can be presented.

The diastereoisomers do not differ greatly in solubility. This possibility seems unlikely, however, since two resolving agents were used without effecting resolution.

It may be possible that only the meso forms were present in solution, the structures of which are given below.



Thirdly, it may be that the bonds are predominantly ionic and that racemization occurs rapidly. This would produce a mixture with statistical distribution of optically active complexes and the meso forms.

Formation constant determinations in progress at the present time indicate that the formation of the  $(\text{Ni}_2 \text{trien}_3)^{+4}$  complex is a two-step reaction. The 1:1 complex forms first which is then changed to the  $[\text{Ni}_2 \text{trien}_3]^{+4}$  complex ion. The most stable binding of two 1:1 complexes to give the  $(\text{Ni}_2 \text{trien}_3)^{+4}$  ion is through the *cis*-positions of the two complexes. This would indicate sp.<sup>3</sup> ionic linkage for the 1:1 complex. This is in line with the observations reported by Dwyer and Mellor.<sup>12</sup>

D. **Magnetic Investigations.** The mass susceptibilities of  $[\text{Ni}_2 \text{trien}_3] \text{Cl}_4$ ,  $[\text{Ni}_2 \text{trien}_3] (\text{NO}_3)_4$ ,

and  $[\text{Ni}_2\text{trien}_3](\text{PtCl}_4)_2$  were determined on a modified Curie-Cheneveau balance.<sup>16</sup>

The measurements were made at 25° using ferrous ammonium sulfate ( $\mu_{\text{eff}} = 5.25$ )<sup>17</sup> as a calibrating agent. From the mass susceptibilities measured at 25° the molecular susceptibility ( $\chi_M$ ) was determined. The effective Bohr magneton numbers were calculated from the formula

$$\mu_{\text{eff}} = 2.83\sqrt{\chi_M T^{18}}$$

The average effective moments per Ni(II) ion were:

$[\text{Ni}_2\text{trien}_3]\text{Cl}_4 = 2.93$	eff. Bohr magneton numbers
$[\text{Ni}_2\text{trien}_3](\text{NO}_3)_4 = 2.91$	eff. Bohr magneton numbers
$[\text{Ni}_2\text{trien}_3][\text{PtCl}_4]_2 = 2.87$	eff. Bohr magneton numbers

This is in good agreement with the values expected for two unpaired electrons in the nickel(II) ion with octahedral valence bond direction.

(16) F. W. Grey and Farquarson, *J. Sci. Inst.*, **9**, 1 (1932).

(17) P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, p. 155.

(18) Ref. 17, p. 79.

**Acknowledgments.**—Mr. N. L. Cull prepared the  $[\text{Ni}_2\text{trien}_3][\text{PtCl}_4]_2$  complex compound. The C, H and N analysis were performed by the Clark Micro Analytical Laboratories, Urbana, Illinois.

### Summary

1. Spectrophotometric investigation of the nickel(II) ion-triethylenetetramine system indicates the existence of the colored  $[\text{Ni}\text{trien}]^{+2}$  and  $[\text{Ni}_2\text{trien}_3]^{+4}$  ions in solution.

2. The following compounds of the  $[\text{Ni}_2\text{trien}_3]^{+4}$  ion were prepared:  $[\text{Ni}_2\text{trien}_3]\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ ,  $[\text{Ni}_2\text{trien}_3](\text{NO}_3)_4 \cdot \text{H}_2\text{O}$  and  $[\text{Ni}_2\text{trien}_3][\text{PtCl}_4]_2$ .

3. It was not possible to isolate any compounds containing the  $[\text{Ni}\text{trien}]^{+2}$  ion.

4. No optically active isomers could be isolated, possibly because of the ionic-metal-to-donor-atom link.

5. Magnetic studies of the compounds of the  $[\text{Ni}_2\text{trien}_3]^{+4}$  ion indicate the existence of two unpaired electrons in the octahedral complex compounds.

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## Inorganic Complex Compounds Containing Polydentate Groups. III. Platinum(II) and Palladium(II) Complexes with Triethylenetetramine<sup>1,2</sup>

BY HANS B. JONASSEN AND N. L. CULL

Elements showing a coordination number of four may form complex compounds with linkages of either the tetrahedral  $sp^3$  or the planar  $dsp^2$  type. The most abundant and satisfactory evidence for the planar structure may be found among the compounds of bivalent platinum and palladium.<sup>3</sup> The alleged resolution of optically active complex compounds of these ions by Reihlen<sup>4</sup> is the only evidence for a possible tetrahedral structure. However, the optical isomer was never obtained free from the resolving agent. Other workers<sup>5,6</sup> were unable to effect any resolution of platinum(II) and palladium(II) complex compounds. Mills and Quibell<sup>7</sup> and Lidstone and Mills<sup>8</sup> successfully resolved bis-chelate complexes of platinum(II) and palladium(II) which would be optically active if the central ion directed its valence forces toward the corners of a planar square or square pyramid. Dipole moment studies, however, completely eliminate the latter possibility.<sup>9</sup>

Magnetic susceptibility measurements of the complexes of bivalent platinum and palladium have shown them to be diamagnetic,<sup>10,11</sup> which constitutes further evidence for planar  $dsp^2$  linkage.<sup>12</sup>

In this investigation triethylenetetramine ( $\text{H}_2\text{NC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2$ ) (abbrev. trien) was used as a coordinating agent for platinum(II) and palladium(II) complex compounds. Since trien acts as a quadridentate group,<sup>13,14</sup> its use offers interesting possibilities because the amine with little difference in strain may assume either a planar or a tetrahedral configuration around the central ion.

In the tetrahedral complex the presence of two unpaired electrons in the  $sp^3$  linkage should produce paramagnetism.<sup>12</sup> Furthermore, if the linkage in the tetrahedral complex were mainly covalent<sup>12</sup> the complex should be capable of resolution since its structure is unsymmetrical.

A planar complex on the other hand would show diamagnetism due to  $dsp^2$  type linkage,<sup>12</sup> and would be non-resolvable.

(1) Based on a portion of the M.S. thesis of N. L. Cull.  
(2) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the 115th National Meeting at San Francisco, March, 1949.

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