The variety of electronic effects expected from this series were uniformly unsuccessful in producing a single carbon-bonded structure. It may be concluded, therefore, that the steric effect of a substituent at this position is more important than the electronic effect in determining the position of keto–enol equilibrium or hybridization. The presence of transoid structures places an oxygen atom within approximate bonding distance of the platinum. Furthermore, it is oriented close to the axis of the d_{xz} or d_{yz} orbitals of the platinum. Since these orbitals are filled, a strong bonding would of course not be expected to occur. However, the symmetry of the crystal field about the platinum, the primary factor in determining electronic transition energies, will have changed drastically. The result of this change is expected to shift electronic transition energies and in fact conforms to the observation that II is green although most platinum complexes are yellow.

The presence of interaction between filled orbitals of the Pt atom and the oxygen atom of a ligand has been demonstrated by Allen and Theophanides for Pt(II) complexes containing α-hydroxyacetylenes.[13] The infrared spectrum of compound II is different from that of compound I in that the former exhibits two extra bands at 1644 and 414 cm^{-1}. These bands may correspond to the stretching and bending of the C=O group perturbed by the interaction with the Pt atom.

(13) A. D. Allen and T. Theophanides, *Can. J. Chem.*, **44**, 2703 (1966).

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Diethylenetriamine Complexes of Platinum(II) Halides

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The major product of a previously described synthesis of [Pt(dien)X]X has been shown to be $Pt_3C_8H_{30}ON_6Cl_8$ for the case where X = Cl. On the basis of both chemical and physical evidence, a structure for the latter is proposed and an alternate procedure for the synthesis of [Pt(dien)Cl]Cl in high yield is described.

In 1934, Mann[1] described a procedure for the synthesis of [Pt(dien)X]X, where dien = diethylenetriamine and X = Br or I but not Cl. For the case where X = Cl, Mann isolated a product to which he assigned the empirical formula $PtC_8H_{30}ON_6Cl_8$ although his analytical data require $Pt_3C_8H_{30}ON_6Cl_8$. Basolo, *et al.*, reported[2] the synthesis of [Pt(dien)Cl]Cl but without details other than the statement that the procedure employed was essentially that described by Mann. However, it was subsequently learned[3] that the method actually used by Basolo and co-workers was closely similar to that devised in this laboratory and described in the present communication. Din and Bailar[4] prepared [Pt(dien)Br]Br in 45% yield by Mann's procedure but it appears that they separated and discarded the more complex halide during the early stages of their synthesis process.

The work described below serves to clarify the nature of $Pt_3C_8H_{30}ON_6Cl_8$ and includes a procedure for the synthesis of pure [Pt(dien)Cl]Cl in high yield.

Experimental Section

Methods.—Infrared spectral data (Table I) were obtained using Beckman IR-7 and IR-11 instruments. Spectra in the 600–4000-cm^{-1} region were taken in KBr pellets and in KI pellets in the 200–700-cm^{-1} region. Typical spectra are shown in Figure 1.

X-Ray diffraction data were obtained using Cu Kα radiation (Ni filter) at 35 kv and 15 ma. Exposure times were 6–12 hr; relative intensities were estimated visually. The *d* spacings corresponding to the most intense lines (with relative intensities in parentheses) are listed immediately following analytical data.

Standard methods of analysis were used in all cases.

Materials.—With the exceptions that follow, all materials used were reagent grade chemicals that were used without further purification.

Solutions of K_2PtCl_4 or $(NH_4)_2PtCl_4$ were prepared as described earlier.[5]

Technical grade dien was purified by distillation in a Nester–Faust annular-spinning-band molecular still. After discarding a yellow low-boiling fraction, a colorless distillate was collected, bp 70–71° (3 mm). For analysis, a sample was converted to the trihydrochloride by treatment with concentrated hydrochloric acid followed by precipitation with ethanol saturated with HCl. The solid was filtered, washed with ethanol, and dried under reduced pressure. *Anal.* Calcd for dien·3HCl: C, 22.60; H, 7.59. Found: C, 22.59; H, 7.65.

Synthesis of $PtI_2 \cdot H_2O$.—A solution of 12.45 g, 0.030 mole, of K_2PtCl_4 in 200 ml of water at 90° was treated with excess KI (15.0 g, 0.09 mole) to precipitate virtually insoluble $PtI_2 \cdot H_2O$ which was separated by filtration, washed with water, and dried in air. (This product resembles finely divided carbon black and is difficult to dry since it invariably migrates from its container when placed in a vacuum desiccator.) The yield was 13.8 g or 98.5% based on K_2PtCl_4. *Anal.* Calcd for $PtI_2 \cdot H_2O$: Pt, 41.78. Found: Pt, 41.53.

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[1] F. G. Mann, *J. Chem. Soc.*, 466 (1934).

[2] F. Basolo, H. B. Gray, and R. G. Pearson, *J. Am. Chem. Soc.*, **82**, 4200 (1960).

[3] F. Basolo, private communication.

[4] B. Din and J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **22**, 241 (1961).

[5] N. G. Kluchnikov and R. N. Savel'eva, *Z. Neorgan. Khim.*, **1**, 2764 (1956).

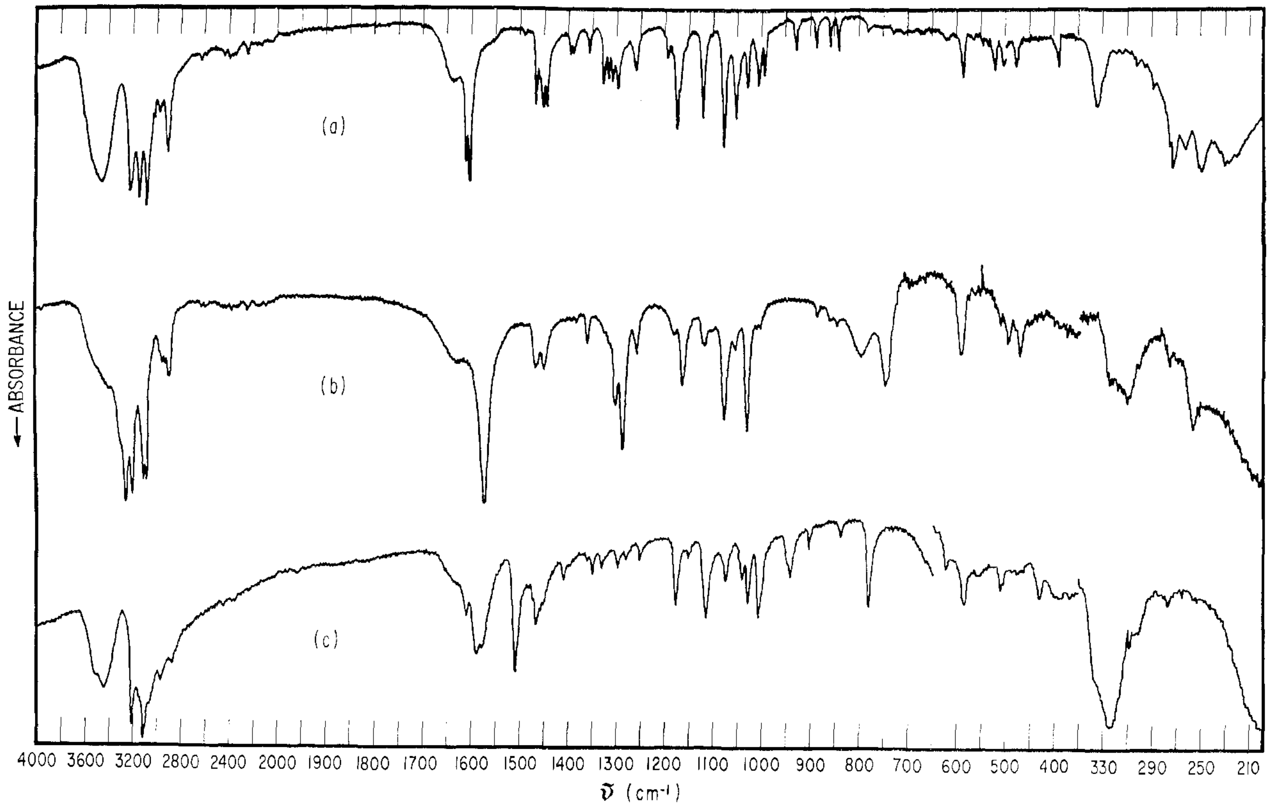

Figure 1.—The infrared spectra of (a) [Pt(dien)Cl]Cl, (b) [Pt(dien)NH_3]$PtCl_4$, and (c) $Pt_3C_8H_{30}ON_6Cl_8$.

Table I

Infrared Spectra in the 200–3800-Cm⁻¹ Region

[Pt(dien)-Cl]Cl	[Pt(dien)-NH_3]$PtCl_4$	$Pt_3C_8H_{30}O$-N_6Cl_8	[Pt(NH_3)$_4$]-$PtCl_4$	Tentative assignments
3450 vs		3450 s	3450 w	ν(OH)
3210 vs	3270 vs	3210 vs		ν(NH_2)
3130 vs	3220 vs			
3070 vs	3120 vs	3120 vs		ν(NH)
	3100 vs	3080 *s, sh*	3290 vs	ν(NH_3)
2970 vw	2970 w	2980 w		ν(CH_2)
2900 s	2900 m	2880 w		
1611 vs		1611 w		δ(NH_2)
1603 vs	1575 vs	1590 s		
			1550 s	δ(NH_3)
		1510 s		δ(NH_3Cl)
1466 s	1470 m	1466 m		δ(NH)
1452 s	1452 m	1455 m, sh		δ(CH_2)
1443 m				δ(NH)
1395 w	1385 vw	1410 vw		ω(CH_2)
1357 w	1362 w	1352 w		ω(NH_2)
			1315 vs	ω(NH_3)
1308 m	1305 s	1300 vw		ω(NH_2)
1298 m	1289 s	1285 vw		γ(CH_2)
1260 w	1260 w	1255 wv		
1175 s	1166 s	1177 m		ω(NH_2)
1125 s	1120 w	1116 m		ν(C–N)
1080 vs	1080 s	1077 w		ν(C–C)
1055 s	1058 w	. . .		ν(C–N)
1032 m	1035 s	1035 m		ν(C–C)
995 m				γ(NH_2)
930 w	. . .	945 w		ν(C–N)
890 w	892 vw	905		ρ(CH_2)
860 w	865 vw	. . .		
842 w	850 vw	843 vw		ν(C–N)
			830 vw	ρ(NH_3)
782 vw	800 m	782 m		ρ(NH_2)
732 vw	747 s			
588 m	592 s	585 m		ν(N′–Pt–N′)
523 w				ν(Pt–N″)
			515 m	ν(Pt–N)
505 vw	499 w	510 w		ν(N′–Pt–N′)
479 w	475 w			δ(NCC)
392 w				
337 s	310 vw[a]	324 vs[a]	310 vs[a]	ν(Pt–Cl)
273 vs	276 vw			δ(N′–Pt–N′)
263 vs	257 w			

[a] Wide band.

Synthesis of [Pt(dien)I]I.—Just enough water was added to 14.0 g (0.030 mole) of $PtI_2 \cdot H_2O$ to form a thick paste; slightly less than a stoichiometric quantity of dien (3.0 ml, 0.027 mole) was added dropwise, with stirring. The resultant gray mixture was baked to dryness on a steam bath overnight. This solid was extracted with water at 90°, unreacted $PtI_2 \cdot H_2O$ was separated by filtration, and the yellow filtrate was evaporated on a steam bath until crystals appeared. The solution was cooled to 5° and the crystalline product was filtered, washed with three 5-ml portions of water, and dried *in vacuo* over KOH for 2 hr. The crystallization process and product recovery were repeated to provide a total yield of 12.7 g (0.023 mole) or 85% based on dien.[6] *Anal.* Calcd for [Pt(dien)I]I: Pt, 35.34; C, 8.70; H, 2.37. Found: Pt, 35.35; C, 8.79; H, 2.52. X-Ray diffraction data: 7.08 (0.3), 5.90 (0.3), 4.47 (1.0), 4.37 (1.0), 4.10 (0.3), 3.83 (0.3), 3.53 (0.8), 2.92 (0.3).

Synthesis of [Pt(dien)Cl]Cl.—To a suspension of 2.21 g (0.0040 mole) of [Pt(dien)I]I in 100 ml of water was added 2.0 g (0.012 mole) of $AgNO_3$ and 3.0 ml of *ca.* 6 *M* HCl solution. This mixture was stirred in the dark for 48 hr and filtered; the clear yellow filtrate was evaporated to 10 ml on a steam bath, then cooled to 5°. The product was filtered, washed with acetone, and dried *in vacuo* for 1 hr over KOH. A second crop of crystals was obtained by dilution of the filtrate with acetone and recovered similarly; the total yield was 1.39 g (0.0038 mole) or 94% based on [Pt(dien)I]I. *Anal.* Calcd for [Pt(dien)Cl]Cl: Pt, 52.85; C, 13.01; H, 3.55. Found: Pt, 52.80; C, 12.95; H, 3.22. X-Ray diffraction data: 6.51 (0.5), 6.28 (0.5), 3.70 (1.0), 3.20 (0.5), 2.64 (0.5).

Synthesis of $Pt_3C_8H_{30}ON_6Cl_8$.—A suspension of 17.6 g (0.0362 mole) of K_2PtCl_6 in 150 ml of water was treated with 1.90 g (0.0181 mole) of $N_2H_4 \cdot 2HCl$ and stirred for 1 hr or until evolution of N_2 subsided. This solution was stirred and heated slowly to 90° to form a clear deep red solution. After cooling to 5°, the solution was filtered and there was no evidence of the presence of either elemental platinum or unreacted K_2PtCl_6. The

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(6) Use of excess dien results in rather intractable oils or gums and lowers the yield to <50%.

filtrate was adjusted to pH 7 with 20% KOH solution, a twofold excess of dien·3HCl (15.4 g, 0.0724 mole) was added, the volume was increased to 300 ml with water, and this mixture was refluxed for 8 hr. The solution was cooled to 5° to provide orange crystals which were filtered, washed with cold (5°) water, and dried *in vacuo* over KOH for 2 hr. The yield was 6.0 g (0.0055 mole) or 46% based on K_2PtCl_6.[7] *Anal.* Calcd for $Pt_3C_8H_{30}ON_6Cl_8$: Pt, 53.44; C, 8.77; H, 2.76; Cl, 25.90. Found: Pt, 53.36; C, 8.85; H, 2.80; Cl, 25.60. X-Ray diffraction data: 7.34 (1.0), 6.00 (1.0), 3.81 (0.5), 3.64 (0.4), 3.53 (0.6). This product was recrystallized from 1 *M* HCl solution; the resulting dark red crystals gave the same analytical and X-ray diffraction data and infrared spectrum as the original orange crystals.

The Action of Aqueous Ammonia on $Pt_3C_8H_{30}ON_6Cl_8$.—About 20 ml of 6 *M* aqueous ammonia was added to 304.3 mg of $Pt_3C_8H_{30}ON_6Cl_8$ and stirred. The solid dissolved, the solution became dark yellow, but after *ca.* 1 min a finely divided pink solid separated. Within 5 min after the addition of the ammonia, the mixture was filtered to provide a clear, colorless filtrate and a pink solid which was washed with water and dried *in vacuo* over KOH for 2 hr. The yield was 87% based on $Pt_3C_8H_{30}ON_6Cl_8$. *Anal.* Calcd for $[Pt(dien)NH_3]PtCl_4$: Pt, 59.83; C, 7.37; H, 2.61; N, 8.59. Found: Pt, 59.71; C, 7.93; H, 2.61; N, 9.03. X-Ray diffraction data: 8.71 (0.5), 6.78 (1.0), 5.60 (0.5), 3.46 (0.6), 3.08 (0.5), 2.92 (0.5).

In two separate but otherwise identical experiments, 0.2778- and 0.7882-mmole samples of $Pt_3C_8H_{30}ON_6Cl_8$ were treated with aqueous ammonia, and the clear, colorless filtrates and washings from the separation of $[Pt(dien)NH_3]PtCl_4$ were analyzed for total Cl^-; the values found were 1.24 and 3.51 mmoles, respectively.

In a third experiment conducted as described above, the clear filtrate was treated with K_2PtCl_4. The resulting pink precipitate gave an infrared spectrum identical with that of $[Pt(dien)NH_3]PtCl_4$. Treatment of this product with 6 *M* aqueous ammonia overnight produced green $[Pt(NH_3)_4]PtCl_4$, which gave an infrared spectrum identical with that described below.

The Action of Aqueous Ammonia on $[Pt(dien)NH_3]PtCl_4$.—A 240-mg (0.368-mmole) sample of $[Pt(dien)NH_3]PtCl_4$ was stirred overnight with 15 ml of 6 *M* aqueous ammonia to form "Magnus' green salt"[8] and a clear, colorless supernatant solution. The solid was filtered, washed with water, and dried in air. The yield was 91.2 mg or 41.3% based on $[Pt(dien)NH_3]PtCl_4$. *Anal.* Calcd for $[Pt(NH_3)_4]PtCl_4$: Pt, 65.02; N, 9.34. Found: Pt, 64.49; N, 9.57. X-Ray diffraction data: 6.25 (1.0), 4.45 (0.6), 2.82 (0.5), 2.13 (0.4). The infrared spectrum for this compound was substantially identical with that included, but without comment or interpretation, in an earlier publication.[9]

A small sample of $[Pt(NH_3)_4]PtCl_4$ was heated in 10 ml of 26% aqueous ammonia to *ca.* 85°. Within 0.5 hr the suspension changed to a clear *colorless* solution. Addition or K_2PtCl_4 resulted in precipitation of green $[Pt(NH_3)_4]PtCl_4$ which had properties identical with those described above.

The Infrared Spectrum of K_2PtCl_4.—For use in the interpretation of other spectral data, the infrared spectrum of K_2PtCl_4 was observed over the range 200–800 cm^{-1}. As expected, this spectrum was relatively simple; the principal features were a very strong broad band at 324 cm^{-1} and a band of weak to medium intensity at 344 cm^{-1}.

Discussion

The present and earlier[1,2,4] experiences with Mann's synthesis of [Pt(dien)X]X show that the desired complexes can be obtained in 35–45% yield where X = Br or I. Where X = Cl the product is a more complex species $Pt_3C_8H_{30}ON_6Cl_8$ which was isolated by Mann but not further investigated. Presumably the formation of an analogous complex could account for the low yields of [Pt(dien)X]X where X = Br or I.

The reaction of dilute aqueous ammonia on $Pt_3C_8H_{30}ON_6Cl_8$ has been shown to proceed as

$$Pt_3C_8H_{30}ON_6Cl_8 + 2NH_3 \xrightarrow{\text{fast}} [Pt(dien)NH_3]PtCl_4 + [Pt(dien)NH_3]Cl_2 + 2HCl + H_2O \quad (1)$$

Compatibility of (1) with the experimental data can be shown as follows. The pink solid product of (1) was obtained in 87% yield and the other product was a clear colorless solution. That the latter contained $[Pt(dien)NH_3]^{2+}$ was shown by

$$[Pt(dien)NH_3]Cl_2 + K_2PtCl_4 \longrightarrow [Pt(dien)NH_3]PtCl_4 + 2KCl \quad (2)$$

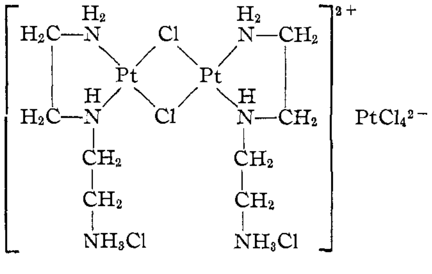
Further, when 304.3 mg (0.2778 mmole) of $Pt_3C_8H_{30}ON_6Cl_8$ was treated with NH_3, 1.24 mmoles of Cl^- was found by analysis as compared with 1.11 mmoles calculated on the basis of (1). This discrepancy, which was observed in independent experiments, can be accounted for on the basis of the 87% yield of $[Pt(dien)NH_3]PtCl_4$ in (1). That this yield was not 100% is attributable to the survival of less than 1 mole of $PtCl_4^{2-}$ from each mole of $Pt_3C_8H_{30}ON_6Cl_8$ used, and the information given above relative to the action of NH_3 on $[Pt(dien)NH_3]PtCl_4$ shows that the loss of $PtCl_4^{2-}$ results from its conversion to $[Pt(NH_3)_4]^{2+}$ by

$$[Pt(dien)NH_3]PtCl_4 + 3NH_3 \xrightarrow{\text{slow}} [Pt(NH_3)_4]PtCl_4 + \text{dien} \quad (3)$$

$$[Pt(NH_3)_4]PtCl_4 + 4NH_3 \longrightarrow 2[Pt(NH_3)_4]Cl_2 \quad (4)$$

and it is the occurrence of (4) that limits the yield in (3) to 47%. The formation of $[Pt(NH_3)_4]^{2+}$ in (4) was confirmed by addition of K_2PtCl_4 to form Magnus' green salt. On this basis, it can be assumed that 1 mole of $PtCl_4^{2-}$ is formed in (1) from 1 mole of $Pt_3C_8H_{30}ON_6Cl_8$ and that 13% of the $PtCl_4^{2-}$ is converted to $[Pt(NH_3)_4]^{2+}$ in the time interval over which (1) was allowed to proceed. Accordingly, the total Cl^- generated *via* (1) is computed as: $4(0.2778) + 0.13 \cdot [4(0.2778)] = 1.25$ mmoles; thus, the 1.24 mmoles of Cl^- accounts for 99.2% of the Cl^- expected. In an independent experiment, 99.5% of the calculated quantity of Cl^- was found by analysis.

The essential features of the structure of the chloro complex can be postulated on the basis of: (1) the chemical evidence given above, (2) maintenance of coordination number 4 for Pt^{2+}, (3) the known bidentate role for dien in relatively strongly acidic solutions, and (4) preference for a five-membered ring over the alternative eight-membered ring.



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[7] When it was found that more of the same product could not be recovered from the filtrate, it was evaporated to 100 ml and treated with KI to form [Pt(dien)I]I. Collectively, the two products thus isolated accounted for 70% of the K_2PtCl_6 used.

[8] G. Magnus, *Pogg. Ann.*, **14**, 242 (1828).

[9] G. M. Barrow, R. H. Kruegger, and F. Basolo, *J. Inorg. Nucl. Chem.*, **2**, 340 (1956).

Support for this structure is also provided by the infrared spectral data listed in Table I; the assignments were made empirically on the basis of published data for $[Pd(dien)Cl]Cl$,[10] $[Pt(NH_3)_4]Cl_2$,[9] $ClCH_2CH_2NH_3Cl$,[11] and the data for K_2PtCl_4 reported herein. The $PtCl_4^{2-}$ unit is characterized by the broad band at 310–320 cm^{-1} as is clearly evident from the spectra shown in Figure 1. Although the very strong broad band at 324 cm^{-1} in the spectrum of the chloro complex is clearly attributable to ν(Pt–Cl), it is not possible to assign ν(Pt–Cl) for the bridging bonds. Either the two are indistinguishable or, more likely, the latter lies below the range of the instrument. The $-CH_2CH_2NH_3Cl$ portion of the proposed structure is responsible for two features of the spectrum of $Pt_3C_8H_{30}ON_6Cl_8$ not found in the spectra of the related compounds shown in Figure 1. The spectra of both the chloro complex and $ClCH_2CH_2NH_3Cl$ show a broadening of the NH_2 stretching bands (3100–3200 cm^{-1}) so as to overlap the CH_2 stretching region 2900–3000 cm^{-1}. The other feature in common is the very strong band at 1510 cm^{-1} which is interpreted as a modified NH_2 bending vibration; the influence of the added mass of the HCl unit should lower the frequency owing to inertial effects.

The OH band at 3450 cm^{-1} cannot be taken as evidence for the presence of H_2O in the chloro complex since it appears, at least at low intensities, in the spectra of the anhydrous salts and is probably an impurity in the KBr used. Otherwise, the assignments given in Table I are entirely consistent with the proposed structure and previously published data.

Acknowledgments.—This work was supported by the U. S. Atomic Energy Commission and the Robert A. Welch Foundation.

[10] G. W. Watt and D. S. Klett, *Spectrochim. Acta*, **20**, 1053 (1964).

[11] "Sadtler Standard Spectra," Sadtler Research Laboratories, Spectrum No. 24369.

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Complexes of the Rare Earths. XI. 2,6-Dicarboxypiperidineacetic Acid

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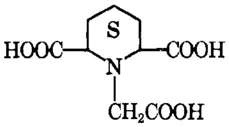
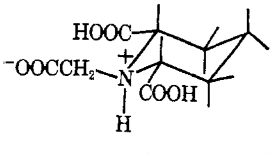
Stepwise formation constants have been determined for the complexes of the rare earth ions and 2,6-dicarboxypiperidineacetic acid at 25° in an aqueous KNO_3 medium (μ = 0.1). Both 1:1 and 2:1 complexes of considerable stability are formed and these are discussed with respect to the corresponding complexes of nitrilotriacetic acid. It is shown that the constraint imposed upon the donor groups by the presence of the piperidine ring is dominant in determining the coordinating properties of 2,6-dicarboxypiperidineacetic acid. Because of this geometrical requirement, the ligand is well suited to form complexes with ions having large coordination numbers, such as the rare earths.



The rare earth ions form both 1:1 and 2:1 complexes of considerable stability with nitrilotriacetic acid (NTA).[2] The common interpretation has been that the formation of these strong complexes involves the interaction of the rare earth ion and all the donor atoms of the ligands in both series of complexes. This, then, leads to the conclusion that the coordination number of the rare earth ions is eight (or larger if water molecules are also involved in the coordination sphere), a conclusion which is now generally accepted.

For a number of years we have been concerned with the affinity of the rare earth ions for a variety of donor atoms, as well as with the rare earth complexes of ligands with stringent geometrical requirements. In this connection we have prepared a new ligand, 2,6-dicarboxypiperidineacetic acid and measured the stability constants of the complexes it forms with a number of divalent metal ions.[3] We wish to report in this article the stability constants of the 1:1 and 2:1 complexes of this ligand and the rare earth ions.



The ligand 2,6-dicarboxypiperidineacetic acid is directly related to NTA with the important modification that a hydrogen atom of each of two methylene groups has been removed and these two groups have

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[1] On leave from The National Chemical Laboratory, Poona, India.

[2] (a) G. Schwarzenbach and R. Gut, *Helv. Chim. Acta*, **39**, 1589 (1956); (b) G. Anderegg, *ibid.*, **43**, 825 (1960).

[3] S. K. Kundra and L. C. Thompson, *J. Inorg. Nucl. Chem.*, in press.