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.

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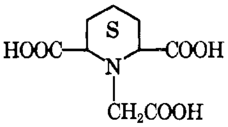
Complexes of the Rare Earths. XI. 2,6-Dicarboxypiperidineacetic Acid

By L. C. THOMPSON and S. K. KUNDRA[1]

Received August 29, 1967

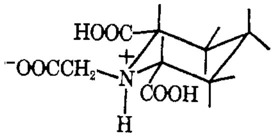
Stepwise formation constants have been determined for the complexes of the rare earth ions and 2,6-dicarboxypiperidineacetic acid



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.

been incorporated into a piperidine ring. Steric arguments and nmr data[4] indicate that the three substituents on the ring are all in equatorial positions. The most important effect on this ligand, as indicated by molecular models, is to constrain the three carboxyl groups so that they are preoriented for chelation.

Experimental Section

Materials and Solutions.—The 2,6-dicarboxypiperidineacetic acid was prepared by the alkaline condensation of 2,6-piperidinedicarboxylic acid with chloroacetic acid as previously described.[3] The rare earth oxides[5] were of 99.9% purity and all other chemicals were of reagent grade. All solutions were prepared and standardized as in earlier work.[6]

Experimental Procedure.—The direct pH method and the tren method previously described were used to determine the stability constants.[6] The concentration of the solutions was kept at 0.001 *M* in each reagent for measurements for the determination of log K_1 and the ligand concentration was increased to 0.002 *M* for those measurements in which data for the 2:1 complexes were taken.[7]

Calculations.—The hand calculations using the tren method with copper as the auxiliary metal ion have been described.[8] The values of log K_1 for lanthanum and of log K_2 for all of the rare earths were determined using the computer program Gauss G on an IBM 1620 computer.[9]

Results and Discussion

The results of the calculations of the formation constants of the 1:1 and 2:1 2,6-dicarboxypiperidineacetic acid–rare earth complexes are given in Table I. All of the calculations were performed using data obtained from pH regions in which there was no interference from hydrolysis either of the metal ion or of the 1:1 complex. In the case of lanthanum the hydrolysis constant of the 1:1 complex was measured and a log *K* value of 9.31 ± 0.05 was found for the reaction $\mathrm{LaXOH^- + H^+ \rightleftharpoons LaX(H_2O)}$. Since all of the calculations were carried out at pH values less than 7, and in most cases less than pH 5, neglect of hydrolysis was justified. It was necessary to use the tren method for all of the 1:1 complexes, except for that of lanthanum, because of the fact that the formation constants were all numerically larger than pk_3.

TABLE I

STABILITY CONSTANTS[a] OF THE RARE EARTH–2,6-DICARBOXYPIPERIDINEACETIC ACID CHELATES AT 25° AND μ = 0.1 (KNO_3)[b]

Metal ion	Log K_1	Log K_2	Log β_2
La^{3+}	9.17	6.17	15.34
Ce^{3+}	9.72	6.65	16.37
Pr^{3+}	10.01	7.04	17.05
Nd^{3+}	10.18	7.32	17.50
Sm^{3+}	10.59	7.77	18.36
Eu^{3+}	10.63	7.91	18.54
Gd^{3+}	10.66	7.96	18.62
Tb^{3+}	10.85	8.04	18.89
Dy^{3+}	10.98	8.13	19.11
Ho^{3+}	11.18	8.17	19.35
Er^{3+}	11.35	8.42	19.77
Tm^{3+}	11.54	8.63	20.17
Yb^{3+}	11.73	8.91	20.64
Lu^{3+}	11.74	8.92	20.66
Y^{3+}	10.83	7.75	18.58

[a] The log K_1 values are considered to be correct within ±0.05 unit (considering the error in the value of the copper complex on which they are based) and the log K_2 values are good to ±0.05 unit at the 95% confidence level. [b] pk_1 = 1.3 ± 0.1; pk_2 = 2.71 ± 0.02; pk_3 = 9.33 ± 0.01.

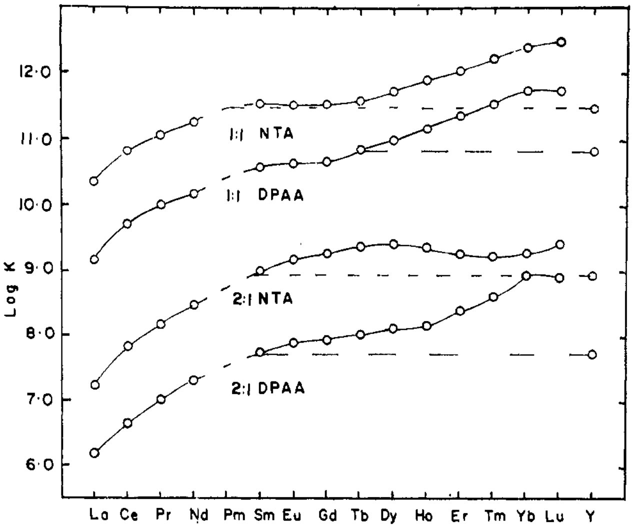

Figure 1.—Plot of stability constants of the 1:1 and 2:1 rare earth–2,6-dicarboxypiperidineacetic acid complexes (DPAA) and NTA complexes.

The values of the formation constants are quite large for a quadridentate ligand and parallel expected behavior to a considerable extent. In Figure 1 we have plotted the stability constants of the 1:1 and 2:1 rare earth complexes of both nitrilotriacetic acid and 2,6-dicarboxypiperidineacetic acid for comparison purposes. There is a general increase in the values of log K_1, and yttrium occupies nearly a "normal" position.[10] The over-all difference between the values for the lanthanum and lutetium chelates is 2.57 log *K* units, whereas the corresponding difference in the nitrilotriacetate complexes is only 2.13 log *K* units.[11] This is reflected in the fact that the difference between the log K_1 values for the corresponding NTA and 2,6-dicarboxypiperidineacetic acid chelates is constant at 1.1 ± 0.1 from lanthanum to neodymium, falls steadily to terbium, and remains at 0.7 ± 0.05 throughout the remainder of the heavy earths. Since NTA contains a more basic site at the nitrogen atom (pk_3 = 9.75 compared to pk_3 = 9.33 for 2,6-dicarboxypiperidineacetic acid), the gross features of this difference are readily apparent. It has been observed previously[3] with the alkaline earth complexes of 2,6-dicarboxypiperidineacetic acid that the smaller ions are stabilized with respect to the larger when the corresponding NTA complexes are con-

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(4) R. A. Martin and L. C. Thompson, unpublished results.

(5) The rare earth oxides were generously supplied by Lindsay Chemical Division, American Potash and Chemical Corp., West Chicago, Ill.

(6) L. C. Thompson, *Inorg. Chem.*, **3**, 1015 (1964).

(7) Tables of experimental data have been deposited as Document No. 9725 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting $3.75 for photoprints, or $2.00 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

(8) H. Ackermann and G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 1543 (1949).

(9) R. S. Tobias and M. Yasudo, *Inorg. Chem.*, **2**, 1307 (1963). We are grateful to Professor Tobias for this program and to Professor D. K. Harriss for modifying it for use on the IBM 1620.

(10) T. Moeller, D. F. Martin, L. C. Thompson, R. Ferrús, G. R. Feistel, and W. J. Randall, *Chem. Rev.*, **65**, 1 (1965).

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sidered. It is apparent again that such an effect, which is most likely due to a more favorable entropy term, is operating in the rare earth complexes so that there is a small stabilization of about 0.4 log K unit for the chelates of the heavier (smaller) rare earth ions.

The magnitude of the stability constants for the 2:1 complexes leaves no doubt as to the fact that all of the groups are coordinated to the metal ion. The existence of only very weak 2:1 complexes with divalent metal ions again points to the larger effective coordination number of the rare earths since the rigidity of the ligand favors coordination of all four donor groups. It is very interesting that the stability constants for the 2:1 complexes show a uniform increase with atomic number. For all other quadridentate ligands of the substituted ammonia type which have been studied, the log K_2 values have decreased rather markedly at some point in the heavy-earth region.[12] (The only exception to this behavior with any quadridentate ligand is with ethylenediamine-N,N′-diacetic acid,[13] and since it is not of the trisubstituted ammonia type, it has rather different steric requirements). This is somewhat surprising since it might have been expected that the bulkiness of the piperidine ring would have led to increased steric factors and thus to a rather marked decrease in log K_2 values somewhere in the heavy-earth region before dysprosium. It should, however, be noted that with 2,6-piperidinedicarboxylic acid,[14] also a molecule with rigid geometric requirements, the log K_2 values for the rare earth ions were larger than expected when compared to those of iminodiacetic acid, a much more flexible molecule. In the 2,6-dicarboxypiperidineacetic acid it appears that the geometric arrangement of the donor groups in an eight-coordinate (or larger) structure is such that the two ligands do not suffer any serious steric hindrance and the normal trend is observed. The lack of steric interference is also shown by the fact that the difference in log K_1 and log K_2 across the series remains nearly constant, as expected for a ligand in which there is no particular steric effect as the size of the metal ion decreases.

Whether or not such steric considerations are the basis for the difference in properties of NTA and 2,6-dicarboxypiperidineacetic acid must, of course, in the final analysis be settled by a direct structure determination. An examination of molecular models of 2,6-dicarboxypiperidineacetic acid and NTA indicates that the former should more readily accommodate the dodecahedral configuration because its basic chelating arrangement is required to form chelating rings of two different sizes. In aqueous solution this would lead to a more favorable entropy term for complexes of this ligand compared to complexes of NTA.

Acknowledgments.—This work was supported by PHS Research Grant GM-08394 from the Division of General Medical Studies, Public Health Service.

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Organosulfur Derivatives of the Metal Carbonyls. X. Some Transition Metal Derivatives Containing Both π-Cyclopentadienyl and *cis*-1,2-Ethylenedithiolate Ligands[1,2]

BY R. B. KING[3] AND C. A. EGGERS[4]

Received September 26, 1967

Reaction between $(C_5H_5)_2MCl_2$ and disodium ethylenedithiolate gives the complexes $(C_5H_5)_2MS_2C_2H_2$ (M = Ti, green-black; M = Zr, orange) suggested to be bis(cyclopentadienyl)metal(IV) ethylenedithiolate complexes from the nmr chemical shifts of the $H_2C_2S_2$ resonances. Reaction between $C_5H_5CoCOI_2$ and disodium ethylenedithiolate gives the volatile purple complex $C_5H_5CoS_2C_2H_2$. Similarly reaction between $[C_5H_5RhBr_2]_n$ and disodium ethylenedithiolate gives the volatile red-green dichroic complex $C_5H_5RhS_2C_2H_2$. The proton nmr chemical shifts of the $H_2C_2S_2$ protons in the $C_5H_5MS_2C_2H_2$ complexes of cobalt and rhodium indicate them to be cyclopentadienylmetal(I) dithioglyoxal complexes. Reaction between $C_5H_5Fe(CO)_2Cl$ and disodium ethylenedithiolate in aqueous methanol gives the black derivative $[C_5H_5Fe(CO)_2]_2S_2C_2H_2$ with a bridging ethylenedithiolate ligand. Reaction between $C_5H_5W(CO)_3Cl$ and disodium ethylenedithiolate gives the purple anion $[C_5H_5W(S_2C_2H_2)_2]^-$ isolable as its tetraphenylarsonium salt.

Introduction

The syntheses of numerous novel metal complexes containing the bis(trifluoromethyl)ethylene dithiolate[5-7] or maleonitriledithiolate[8,9] ligand have been investigated in considerable detail. However, syntheses of similar metal complexes containing the unsub-

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[1] Portions of this work were presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

[2] Part IX: R. B. King and M. B. Bisnette, *Inorg. Chem.*, **6**, 469 (1967).

[3] Fellow of the Alfred P. Sloan Foundation, 1967–1969.

[4] Postdoctoral Research Associate, Jan–Oct 1967.

[5] R. B. King, *J. Am. Chem. Soc.*, **85**, 1587 (1963).

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[9] J. Locke and J. A. McCleverty, *Inorg. Chem.*, **5**, 1157 (1966).