lium ions,[27] which will penetrate to a greater average distance from the actual particle track, and so lead to a slightly greater dispersion of the initial radical positions around the track. Thus, comparing a helium ion with a deuteron having the same linear energy transfer, the actual mean initial volume density of radicals will be somewhat greater along the track of the deuteron.

A calculation of the competition, in the expanding track, between radical recombination and capture by such active solutes as ferrous sulfate and oxygen is too complicated to be carried out rigorously. The most elaborate attempt at an approximate computation is that of Ganguly and Magee.[28] They found it necessary to assume, among other approximations that the concentration of the scavenger solutes remained constant at all points throughout the expanding track. This assumption can hardly be true for tracks of moderately high LET, since it is readily calculated from their own figures that the initial mean radical concentration in the track of a 36-Mev. helium ion is about 0.15 *M*, which is orders of magnitude higher than the concentrations of ferrous sulfate and oxygen used as scavengers in this work. The scavengers will then be entirely depleted near the center of the track, where a large fraction of the molecular products are formed. The calculations of Ganguly and Magee therefore underestimate the fraction of radicals combining with one another, and the error should increase with increasing LET. Comparison with experiment is also confused by the fact that two kinds of radicals are in fact formed, while Ganguly and Magee assumed the radicals to be all alike, and calculated only a quantity S, the fraction of all radicals which react with scavengers. We have compared the ratio of our yields for H atoms and molecules, $G_H/2G_{H_2}$, with their calculated values of $S/(1 - S)$. The results showed that the change in radical yield with LET was somewhat faster than predicted for a given concentration of scavengers, as expected on account of neglect in the calculations of scavenger depletion in the track.

The change of radical yield with scavenger concentration, as shown in our experiments by the effect of oxygen concentration on the ferrous oxidation yields, seems to be of about the magnitude predicted by Ganguly. The effect of ferrous ion concentration on the oxidation yield must be interpreted as an increase in total net water decomposition caused by greater scavenging of the OH radicals by the ferrous ions. It thus appears that in general the system conforms to the predictions of the theory, and that closer agreement with experiment would be expected if calculations were to take into account the depletion of solute concentration within the expanding track.

There is however one feature of the present results which does not appear to conform to expectations. The net water decomposition appears to change very little or not at all over the range of LET's from zero energy up to 38-Mev. helium ions, in which range the hydrogen yield G_{H_2} changes by about 0.5. In passing over the rest of the range from 38-Mev. helium ions up to fast electrons we find that the hydrogen yield undergoes a further drop of about 0.6 while the net water decomposition increases by 1.0. According to the free radical theory, the yields of hydrogen and net water decomposition should change in a smoothly complementary manner. A possible explanation for the discrepancy would be that an extra source of water decomposition exists which comes into play with especial prominence in dense radical tracks and thus counterbalances the increased recombination of radicals to water which is expected in such tracks. The extra source of water decomposition might consist of a species of excited water molecules which normally decay without decomposition, and produce net chemical reaction only if formed in adjacent sites; or they might be regarded as H-OH radical pairs formed together (in a "cage") which normally recombine rapidly, and can react with one another to form H_2 and H_2O_2 molecules only if formed in adjacent sites. Further work is needed on determination of the net water decomposition yields under different conditions at moderate to high LET's.

UPTON, N. Y.

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[27] E. Pollard, *Advances in Biol. and Med. Phys.*, **3**, 153 (1953).

[28] A. K. Ganguly and J. L. Magee, *J. Chem. Phys.*, **25**, 129 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF SYDNEY]

Sexadentate Chelate Compounds. IX

BY FRANCIS LIONS AND KENNETH V. MARTIN[1]

RECEIVED OCTOBER 2, 1956

1ε,3ε,5ε-Triaminocyclohexane has been prepared by an improved process and condensed with salicylaldehyde and pyridine-2-aldehyde, giving 1ε,3ε,5ε-tris-salicylideneaminocyclohexane and 1ε,3ε,5ε-tris-(α-pyridylmethyleneamino)-cyclohexane, respectively. Each of these condensation products has been shown to be capable of functioning as a sexadentate chelate compound of novel type.

The ability of an organic compound to function as a sexadentate chelate compound, whose molecule can supply six donor atoms to occupy without undue strain the six octahedrally disposed coördination positions about a six-covalent metal atom, depends upon the manner of construction of the molecule, on the nature of the atoms which function as donor atoms, and on the nature of the metal atom. Three different types of sexadentate chelate compound appear, so far, to have been prepared and studied. The first of these, shown diagrammatically in Fig. 1a, may be considered as

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having the donor atoms as members of a chain.[2] The second, of which ethylenediaminetetraacetic acid may be considered the prototype, has a doubly-bifurcated chain, with branching occurring at two of the donor atoms (Fig. 1b). The third type, mentioned in Part I of this series of papers, and of which an example is more fully described in Part VIII, has four of its donor atoms in a normal chain and the other two in a branch chain, the bifurcation here occurring at an atom other than one of the donor atoms (Fig. 1c).

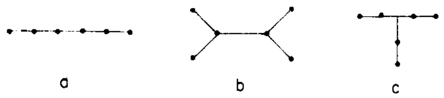

Fig. 1.

It is possible to devise other arrangements with different dispositions of the donor atoms and there seems little reason to doubt that substances with molecules of such new types will eventually be synthesized and will function as sexadentates. In this paper we describe some sexadentate chelate compounds of quite novel molecular type which were deliberately designed after theoretical consideration of the stereochemistry of cyclohexane derivatives. Their ability to function as sexadentates is at once a confirmation of cyclohexane stereochemical theory and of the theory of octahedral disposition of donor atoms about a six-coördinated metal atom in coördination compounds.

Hassell and Lunde[3] in 1950 produced a 1,3,5-triaminocyclohexane in low yield by sodium and alcohol reduction of 1,3,5-cyclohexan-trione trioxime (phloroglucinol trioxime) and showed by comparison of its X-ray powder diagrams with those of α-phloroglucitol dihydrate that it is the *cis* compound—$1\epsilon,3\epsilon,5\epsilon$-triaminocyclohexane (I). According to cyclohexane stereochemical theory the three nitrogen atoms in a molecule of it would, normally, all be situated in the equatorial plane (Fig. 2a) of a "chair" form. Transformation of this "chair" form into the alternative "chair" form would bring each of the nitrogen atoms into the axial position (Fig. 2b). Examination of models shows that it should be relatively easy simultaneously to unite three atoms in these positions (such as the amino nitrogens) to a single suitable multivalent atom with three available pyramidally directed valences (Fig. 3a). The resultant molecular arrangement would constitute a type of cage-ring structure of essentially similar type to that present in hexamethylenetetramine (Fig. 3b).

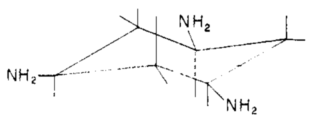

Fig. 2a.

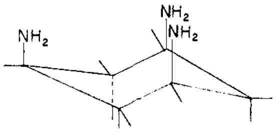

Fig. 2b.

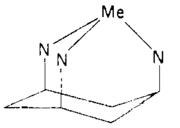

Fig. 3a.

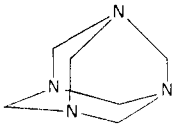

Fig. 3b.

After our work had commenced, Stetter and Steinacher[4] published results showing that *cis*-phloroglucitol can be made readily to form a series of cyclic ortho esters (2,4,10-trioxaadamantanes) of the general formula shown in Fig. 4, which is structurally analogous to Figs. 3a and 3b.

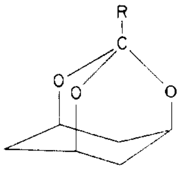

Fig. 4.

We have greatly improved the preparation of I from phloroglucinol trioxime by making use of the Birch reduction.[5] Condensation of I with freshly distilled pyridine-2-aldehyde (3 moles) in boiling ethanol for five minutes gave crude oily $1\epsilon,3\epsilon,5\epsilon$-tris-($\alpha$-pyridylmethyleneamino)-cyclohexane (II), which reacted readily with an aqueous iron(II) sulfate solution to give a mulberry-red solution. Addition to this of a soluble perchlorate precipitated the complex 1a,3a,5a-tris-(α-pyridylmethyleneamino)-cyclohexane-iron(II) perchlorate (III). This salt is diamagnetic—behavior characteristic of an octahedral iron(II) complex with $3d^24s4p^3$ lower level covalent bonds. It is a typical ternary electrolyte. The constitution of its complex cation is shown by the partial diagram of Fig. 5, which, for clarity, shows only two pyridylmethylene residues and does not show hydrogen atoms.

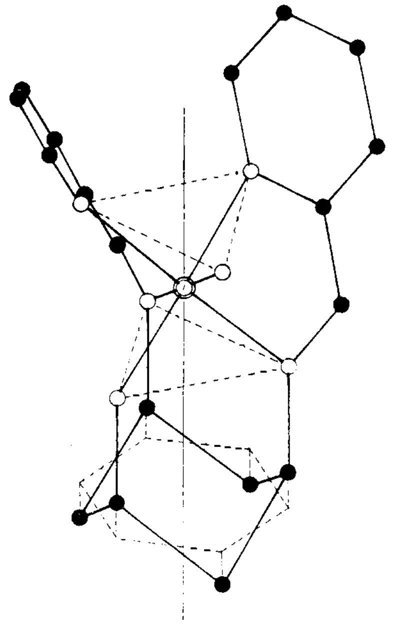

Fig. 5.

Coördination of a molecule of II as a sexadentate molecule with a metal atom requires as a preliminary that the "chair" form of the cyclohexane ring

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(2) Lims, *et al.*, **79**, 1269(1957).

(3) O. Hassell and K. Lunde, *Research* (*London*), **3**, 484 (1950).

(4) H. Stetter and K. H. Steinacher, *Chem. Ber.*, **86**, 790 (1953).

(5) *Cf. e.g.*, A. J. Birch, *Quart. Revs.*, IV, 69 (1950).

with equatorial nitrogen atoms at the 1,3,5-positions be transposed to the alternative "chair" form, thus bringing the nitrogen atoms into axial positions. These three nitrogens then become located at the angles of an equilateral triangle (which constitutes one face of the coördination octahedron) and bonded to the same metal atom above the plane of the triangle along axes originating at the metal atom and mutually at right angles to each other. To each of these nitrogen atoms is attached an α-pyridylmethylene group, and the three nitrogens of the pyridine nuclei, constituting as they do the other three donor atoms of the coordinating sexadentate molecule, lie also at the angles of an equilateral triangle beyond the metal atom and parallel to the first triangle. This second triangle also constitutes a face of the coördination octahedron, but it is so located that each of its angles is directly opposite the middle of a side of the first triangle. Since each nitrogen of this first triangle is linked to a nitrogen atom of the second triangle, a little consideration will show that these organic linking chains must be arranged in a partially spiral manner (one-sixth of a revolution) along an axis at right angles to both the triangular faces. Such a partial spiral may be either right-handed or left-handed and the molecular arrangement must be dissymmetrical. It does contain one triad axis of symmetry and models show that the complex ion is shaped somewhat like a three-bladed propeller. In consequence, III should exist in enantiomorphic forms, Fig. 5 representing (partially) one of these forms.

Soluble complex iron(II) salts containing the same complex cation as is present in III can be oxidized in solution by cerium(IV) nitrate to the deep blue iron(III) complex salts and a blue solid perchlorate can be precipitated. However, it rapidly turns red on exposure to air and could not be obtained analytically pure, apparently reverting to the iron(II) complex salt. There would thus appear to be a considerable degree of stabilization of the iron(II) state in these salts—a fact which might well be correlated with the arrangement of the donor atoms of the three pyridine nuclei along axes intersecting at the metal atom and mutually at right angles to each other.[6]

Interaction of II and cobalt(II) chloride in ethanol gave a brown-pink solution from which the crystalline 1a,3a,5a-tris-(α-pyridylmethyleneamino)-cyclohexane-cobalt(II) perchlorate (IV) could be precipitated. IV had a magnetic moment of 4.7 Bohr magnetons, consistent with that of a cobalt(II) octahedral complex utilizing $4s4p^3 4d^2$ upper level covalent bonds. Oxidation of this complex cobalt(II) salt could be carried out only with difficulty and over a prolonged period of time. Even so strong an oxidizing agent as cerium(IV) nitrate failed to effect immediate oxidation. However, treatment with hydrogen peroxide solution for a week was successful, a violet-colored crystalline diamagnetic 1a,3a,5a-tris-(α-pyridylmethyleneamino)-cyclohexane-cobalt(III) perchlorate being gradually precipitated.

The intense colors exhibited by the complex iron(II), cobalt(II) and cobalt(III) salts derived from II make difficult studies designed to effect their resolution. In an endeavor to overcome this, 1a,3a,5a-tris-(α-pyridylmethyleneamino)-cyclohexane-rhodium(III) perchlorate (V) has been prepared as a practically colorless microcrystalline compound. Unfortunately, because of the inability of K.V.M. to continue with this work, we are unable to report its resolution.

The base I condenses readily with salicylaldehyde (3 moles) to give crystalline 1ε,3ε,5ε-tris-(salicylideneamino)-cyclohexane (VI). This reacted readily in methanol with a methanol solution of cobalt(II) acetate to give an unstable cobalt(II) complex which was readily oxidized to the stable 1a,3a,5a-tris-(salicylideneamino)-cyclohexane-cobalt(III) (VII), a red-brown relatively infusible chloroform-soluble solid with the anticipated composition and molecular weight. Its stereochemical structure should be similar to that ascribed to the complex cation of III. Similarly, 2-naphthol-1-aldehyde reacted with I to give 1ε,3ε,5ε-tris-(2′-hydroxy-1′-naphthylmethyleneamino)-cyclohexane, which was obtained as a yellow crystalline hydrate. From it could be prepared the fusible sesquihydrate of 1a,3a,5a-tris-(2′-hydroxy-1′-naphthylmethyleneamino)-cyclohexane-cobalt(III), an inner complex constituted similarly to VII.

Experimental

1ε,3ε,5ε-Triaminocyclohexane (I).—1,3,5-Cyclohexanetrione trioxime (10 g.)[7] was finely powdered and dissolved in liquid ammonia (600 ml.). Absolute ethanol (70 ml.) was then added, followed by thinly-sliced sodium (25 g.) which was added as rapidly as possible. After 10 minutes a grey solid had separated. The sodium dissolved completely in about 15 minutes. Water (20 ml.) was then cautiously added and the precipitated solid was filtered, washed with liquid ammonia (300 ml.) and discarded. The combined filtrates were evaporated and the dark aqueous residue made strongly alkaline with sodium hydroxide. It was then continuously extracted with ether for three hours. After drying over anhydrous magnesium sulfate and removal of the ether the residual oil was distilled *in vacuo*. It came over as a colorless oil (4 g., 57%), b.p. 110° (2.7 mm.), and on long standing it solidified. For analysis it was converted into its tris-hydrochloride, colorless needles, m.p. 320° (from ethanol–water).

Anal. Calcd. for $C_6H_{18}N_3Cl_3,H_2O$: C, 28.1; H, 7.9. Found: C, 28.2; H, 7.8.

1ε,3ε,5ε-Tris-(salicylideneamino)-cyclohexane (VI).—Salicylaldehyde (9 g., 3 moles) was added to a solution of I (3 g.) in ethanol (20 ml.) and the solution boiled under reflux for 5 minutes. On cooling, a bright yellow crystalline solid (7.5 g.) separated. Recrystallized from ethanol–ethyl acetate it was obtained in yellow needles, m.p. 167°.

Anal. Calcd. for $C_{27}H_{27}N_3O_3$: C, 73.5; H, 6.1. Found: C, 73.3; H, 6.1.

1a,3a,5a-Tris-(salicylideneamino)-cyclohexane-cobalt(III) [VII].—The Schiff base VI (1 g.) was dissolved in ethyl acetate (10 ml.) and a solution of cobalt(II) acetate tetrahydrate (0.5 g.) in methanol (20 ml.) added. The cobalt (II) complex precipitated immediately as a pale orange solid which darkened on exposure to air. Hydrogen peroxide solution (5 ml. of 3%) was added and the mixture heated to boiling on the water-bath for 5 minutes. The solution and the suspended solid became much darker in color. Water was added and the mixture was then extracted with chloroform (3 lots of 100 ml.). The combined extracts were washed several times with water, dried over anhydrous sodium sulfate, and then reduced in volume to 10 ml. The cobalt(III) complex (0.4 g.) which came out was recrystal-

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[6] *Cf.* G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940).

[7] A. Baeyer, *Ber.*, **19**, 159 (1886).

lized from chloroform and obtained in red-brown prisms which did not melt below 360°.

Anal. Calcd. for $C_{27}H_{24}O_3N_3Co$: C, 65.2; H, 4.9; N, 8.4; Co, 11.8; mol. wt., 497. Found: C, 64.8; H, 5.0; N, 8.1; Co, 11.8; mol. wt. (Rast, in camphor), 500.

1a,3a,5a-Tris-(α-pyridylmethyleneamino)-cyclohexane Iron(II) Perchlorate (III).—Freshly distilled pyridine-2-aldehyde (2.8 g., 3 moles) was added to a solution of the base I (1.15 g., 1 mole) in ethanol (15 ml.) and the solution refluxed on the water-bath for 5 minutes. The odor of pyridine-2-aldehyde had then disappeared and the color was deep yellow. A solution of iron(II) sulfate heptahydrate (1.3 g., 1 mole) in water (5 ml.) was added, the color at once becoming deep mulberry-red. After addition of perchloric acid (5 ml. of 10%) and cooling the complex iron(II) perchlorate (3 g.) crystallized out. Recrystallized from hot water it formed glistening red plates, m.p. 260° (with violent dec.).

Anal. Calcd. for $C_{24}H_{24}N_6O_8FeCl_2$: C. 44.2; H, 3.7; N, 12.9; Fe, 8.6; mol. wt., 650. Found: C, 44.1; H, 3.9; N, 12.8; Fe, 8.4; mol. wt. (ebullioscopically in water, for ternary electrolyte), 624; mol. cond., 246 mhos.

The compound is diamagnetic.

1a,3a,5a-Tris-(α-pyridylmethyleneamino)-cyclohexane-cobalt(II) Perchlorate (IV).—Freshly distilled pyridine-2-aldehyde (2.3 g., 3 moles) was added to a solution of I (1.0 g., 1 mole) in ethanol (10 ml.) and the solution heated gently under reflux for 5 minutes. A solution of cobalt(II) chloride hexahydrate (1.8 g., 1 mole) in ethanol (20 ml.) was then added. The resulting deep blood-red solution was concentrated to small bulk and a solution of perchloric acid (10 ml. of 10%) added. The brownish-pink complex cobalt(II) salt which crystallized was recrystallized from boiling water and obtained in brownish-pink needles, m.p. 280° dec.

Anal. Calcd. for $C_{24}H_{24}N_6O_8Cl_2Co$: C, 44.0; H, 3.7; N, 12.8; Co, 9.0. Found: C, 44.0; H, 3.9; N, 12.6; Co, 8.9.

The compound was paramagnetic with a magnetic moment of 4.73 Bohr magnetons at 22°.

1a,3a,5a-Tris-(α-pyridylmethyleneamino)-cyclohexane-cobalt(III) Perchlorate.—The above-described salt IV (0.3 g.) was dissolved in boiling water (20 ml.) and to the solution, carefully cooled so as to avoid crystallization, were added solutions of hydrogen peroxide (5 ml. of 3%) and perchloric acid (5 ml. of 10%). No immediate change in color was discernible. After standing at room temperature for a week the color had changed to mauve and the complex cobalt(III) salt had separated as a violet solid (0.15 g.). It was recrystallized from hot water and obtained in violet plates which did not melt at 300°.

Anal. Calcd. for $C_{24}H_{24}N_6O_{12}Cl_3Co$: C, 38.3; H, 3.2; Co, 7.9. Found: C, 38.6; H, 3.5; Co, 7.8.

The substance is diamagnetic.

1ε,3ε,5ε-Tris-(2′-hydroxy-1′-naphthylmethyleneamino)-cyclohexane Monohydrate.—I (1 g.) was added to a solution of 2-hydroxy-1-naphthaldehyde (2 g.) in ethanol (10 ml.). A deep yellow color developed immediately. After heating at the boiling point for 10 minutes the solution was cooled to 0°. The oil which separated soon solidified after addition of water (1 ml.). Recrystallized from aqueous ethanol it was obtained as a yellow powder, m.p. 165° (with previous softening at 150°).

Anal. Calcd. for $C_{39}H_{33}O_3N_3 \cdot H_2O$: C, 76.8; H, 5.7; N, 6.9. Found: C, 76.9; H, 5.6; N, 7.1.

1a,3a,5a-Tris-(2′-hydroxy-1′-naphthylmethyleneamino)-cyclohexanecobalt(III) Sesquihydrate.—The method was similar to that used in preparing VII. The substance crystallized from chloroform–methanol in brown microcrystals, m.p. 253°.

Anal. Calcd. for $C_{39}H_{30}N_3O_3Co \cdot 1^1/_2H_2O$: C, 69.4; H, 4.9; Co, 8.8. Found: C, 69.4; H, 4.7; Co, 8.6.

1a,3a,5a-Tris-(α-pyridylmethyleneamino)-cyclohexane-rhodium(III) Perchlorate.—I (0.4 g.) and freshly distilled pyridine-2-aldehyde (0.9 g.) were heated together at 95° for 5 minutes, then rhodium(III) chloride (0.6 g.) was added and the heating continued for 20 minutes. The grey solid which precipitated on addition of dry ether (20 ml.) was collected and dissolved in water (10 ml.). Saturated aqueous sodium perchlorate solution (5 ml.) was added, and the precipitated complex rhodium(III) perchlorate collected and recrystallized from water. It was thus obtained in grey microcrystals.

Anal. Calcd. for $C_{24}H_{24}N_6RhCl_3O_{12}$: C, 36.1; H, 3.0; Rh, 12.9. Found: C, 35.6; H, 3.4; Rh, 12.3.

Acknowledgment.—The authors gratefully acknowledge the assistance of Miss B. Stevenson, who carried out all the C, H and N microanalyses.

SYDNEY, AUSTRALIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Infrared Absorption Spectra of Inorganic Coördination Complexes. X. Studies of Some Metal–Urea Complexes[1a,b]

BY R. B. PENLAND, S. MIZUSHIMA,[1c] COLUMBA CURRAN AND J. V. QUAGLIANO

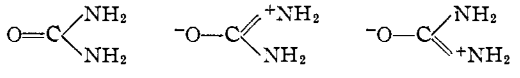
RECEIVED AUGUST 30, 1956

Infrared spectra of some urea–metal complexes have been measured in the 2–35 μ region. From a comparison with the result of the calculation of the normal vibrations of urea, the absorption bands observed in the metal–urea complexes have been assigned. The spectra reveal that urea forms nitrogen-to-metal bonds with Pt(II) and Pd(II), and oxygen-to-metal bonds with Cr(III), Fe(III), Zn(II) and Cu(II).

Introduction

Stable complexes formed from metal salts with 2, 4 or 6 moles of urea are known. However, the inner structures of these complex salts have not been determined.

Vaughan and Donohue[2] considered the structure of urea to involve resonance between the three following structures, the observed values of the interatomic distance indicating 30% double bond character for the carbon-to-nitrogen bonds leaving 40% for the carbon-to-oxygen bond. Kumler[3]



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[1] (a) Paper IX in series, scheduled to appear March, 1957, in *Spectrochim. Acta*, in press. (b) Abstracted from a portion of the Ph.D. thesis of R. B. Penland, Notre Dame, June, 1956. Presented before the Physical and Inorganic Division of the American Chemical Society, Minneapolis, Minnesota, September, 1955. Supported in part under A.E.C. Contract AT(11-1)-38, Radiation Project of the University of Notre Dame. (c) Visiting Professor, Faculty of Science, Tokyo University.

[2] P. Vaughan and J. Donohue, *Acta Cryst.*, **5**, 530 (1952).

[3] W. D. Kumler and G. M. Fohlen, THIS JOURNAL, **64**, 1944 (1942).