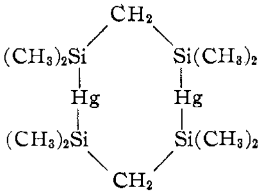

In this reaction 2.499 g of pure product was isolated. This corresponds to a yield of 56% based upon the amount of 2,4-dichloro-2,4-dimethyl-2,4-disilapentane used.

Photolysis of 2,2,4,4,6,6,8,8-Octamethyl-2,4,6,8-tetrasila-1,5-dimercuracyclooctane.—A solution prepared by mixing 0.7106 g (1.07 mmol) of 2,2,4,4,6,6,8,8-octamethyl-2,4,6,8-tetrasila-1,5-dimercuracyclooctane with 10 ml of *n*-pentane sealed in an evacuated Pyrex vessel was irradiated by a commercial sunlamp for 5 days. Initially some yellow crystalline solid was present due to the limited solubility of the cyclic dimercurial in *n*-pentane. During the course of the irradiation this solid dissolved to form a clear colorless solution and a bead of mercury. When no further change could be noted, the reaction tube was opened and the solvent was removed. Remaining behind was 4.1 g (2.03 mmol) of mercury, 96% of the amount expected from eq 2, and 0.237 g of a white crystalline solid identified as 1,1,2,2,4,4,5,5-octamethyl-1,2,4,5-tetrasilacyclohexane by its analysis and melting point of 48.8-50.0° (lit. mp 42°,[14] 51-52°[15]). *Anal.* Calcd for $[C_5H_{14}Si_2]_n$: C, 46.1; H, 10.85; Si, 43.1. Found: C, 46.3; H, 10.56; Si, 42.9. The amount of this cyclotetrasilane isolated is 85% of that expected from eq 2.

Other physical data were obtained for this previously reported compound. Nmr spectrum (in methylene chloride): τ 9.91, 10.10, area ratio 6.3:1 (expected 6.0:1). Mass spectrum [m/e (relative per cent)]: M, 260 (5.6); M–CH_3, 245 (4.4); M–Si$(CH_3)_3$, 187 (1.9); Si$(CH_3)_3$, 73 (100). Infrared spectrum (cm^{-1}) (CsBr): 2950 (m), 2890 (m, sh), 2860 (m, sh), 1400 (m), 1350 (m), 1250 (m), 1245 (m, sh), 1023 (m), 830 (s, sh), 810 (s), 789 (s, sh), 740 (w), 683 (w), 665 (w), 622 (w), 575 (w).

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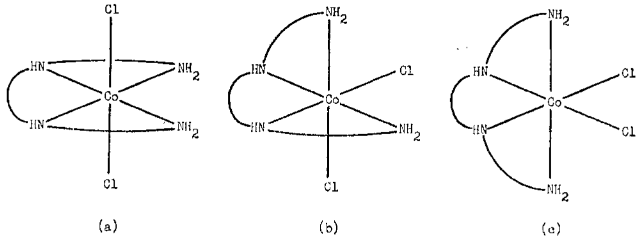
Stereospecific Isomerization of Some Cobalt(III) Complexes with Flexible Tetramine Ligands

BY GEORGE R. BRUBAKER AND DAVID P. SCHAEFER

Received April 21, 1970

In the course of a continuing study of the stereochemistry of various cobalt(III) complexes with flexible tetradentate ligands,[1] we have reexamined the complexes *trans*-dichloro(3,7-diaza-1,9-diaminononane)cobalt(III) perchlorate (*trans*-$[Co(2,3,2\text{-tet})Cl_2]ClO_4$) and *trans*-dichloro(4,7-diaza-1,10-diaminodecane)cobalt(III) perchlorate (*trans*-$[Co(3,2,3\text{-tet})Cl_2]ClO_4$) described by Hamilton and Alexander.[2,3] We have extended this series to several mixed-ligand complexes with bidentate ligands, including the oxalate dianion. Three topological isomers are possible for the diacidotetramine complexes (Figure 1), though not all have yet been observed; of these, the two *cis* forms should exist for the oxalato complexes.



(a) (b) (c)

Figure 1.—The geometrical isomerism of flexible tetramine ligands: (a) *trans;* (b) β or unsymmetrical *cis;* (c) α or symmetrical *cis*.

The complexes $Co(2,3,2\text{-tet})OX^+$, and $Co(3,2,3\text{-tet})OX^+$ may be prepared from the corresponding *trans*-dichloro derivatives by the action of concentrated aqueous oxalic acid. The optical antipodes of these mixed-ligand oxalatotetramine complexes may be separated by fractional crystallization of the monohydrogen bis(benzoyl)-*d*-tartrate salts.

We have assigned the β-*cis* configuration to the complex $Co(2,3,2\text{-tet})OX^+$ and the α-*cis* configuration to the complex $Co(3,2,3\text{-tet})OX^+$ by comparing the ORD curves of these complexes (Figure 2) with those of the

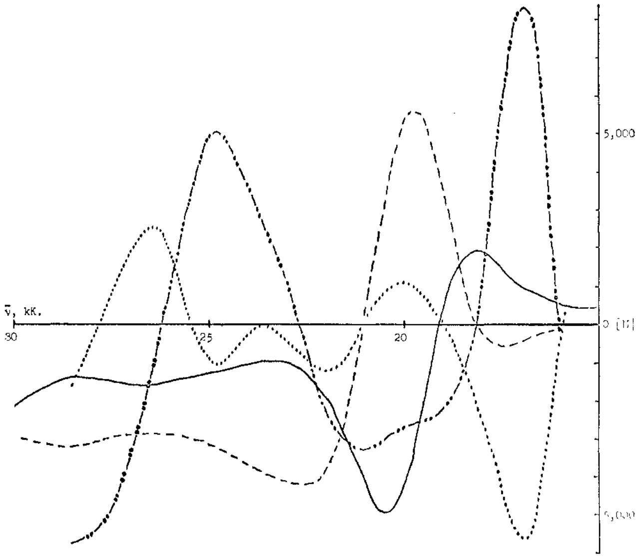


Figure 2.—The optical rotatory dispersion (15–30 kK) of Λ-β-(*RR*)-$Co(2,3,2\text{-tet})OX^+$ (———), Λ-α-(*RR*)-$Co(3,2,3\text{-tet})OX^+$ (– – – – –), *trans*-(*RR*)-$Co(2,3,2\text{-tet})Cl_2^+$ (×10) (–··–··–··–), and *trans*-(*RR*)-$Co(3,2,3\text{-tet})Cl_2^+$ (×5) (········).

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[2] H. G. Hamilton and M. D. Alexander, *Inorg. Chem.*, **5**, 2060 (1966).

[3] M. D. Alexander and H. G. Hamilton, *ibid.*, **8**, 2131 (1969).

known isomers of the triethylenetetramine complex Co(trien)OX$^+$.[4] To demonstrate the correctness of our assignments of configuration, we have followed the procedure of Buckingham, Marzilli, and Sargeson,[5] converting each optically active oxalatotetramine complex into the corresponding *trans*-dichlorotetramine derivative. The preference of the tetramines 2,3,2-tet and 3,2,3-tet for the *trans* configuration facilitates this transformation in the acidic medium required for retention of configuration at the coordinated secondary amine nitrogen atoms. We have assigned the absolute configurations to the *trans*-dichlorotetramine complexes by comparing their ORD and CD curves with those of the known triethylenetetramine complexes. The configurations of this family of complexes are related by the scheme

$$\underset{[M]_D\ =\ +880^\circ}{\Lambda\text{-}\beta\text{-}(SS)\text{-}[Co(trien)Cl_2]ClO_4} \xrightleftharpoons[\text{reflux 30 min}]{BH_3OH\text{-}HCl} \underset{[M]_D\ =\ +3000^\circ}{trans\text{-}(SS)\text{-}[Co(trien)Cl_2]ClO_4}$$

$$\underset{[M]_{503}\ =\ +5050^\circ}{\Lambda\text{-}\beta\text{-}(RR)\text{-}[Co(2,3,2\text{-}tet)OX]ClO_4} \xrightleftharpoons[H_2C_2O_4]{HCl} \underset{[M]_D\ =\ -880^\circ}{trans\text{-}(RR)\text{-}[Co(2,3,2\text{-}tet)Cl_2]ClO_4}$$

$$\underset{[M]_{521}\ =\ -5000^\circ}{\Lambda\text{-}\alpha\text{-}(RR)\text{-}[Co(3,2,3\text{-}tet)OX]ClO_4} \xrightleftharpoons[H_2C_2O_4]{HCl} \underset{[M]_D\ =\ +390^\circ}{trans\text{-}(RR)\text{-}[Co(3,2,3\text{-}tet)Cl_2]ClO_4}$$

It has been shown that the configuration of the coordinated secondary nitrogen atoms control the course of the interconversion of *trans*-Co(trien)Cl$_2^+$ and β-*cis*-Co(trien)Cl$_2^+$, which involves the shift of one donor atom.[5] The interconversion of *trans*-Co(3,2,3-tet)Cl$_2^+$ and α-*cis*-Co(3,2,3-tet)OX$^+$ is the only example known to us in which the configuration of the secondary amine groups controls the stereochemistry of the shift of *two* donor atoms. In contrast with the chemistry of cobalt(III) complexes with triethylenetetramine, we find that the oxalato and dichloro 2,3,2-tet and 3,2,3-tet complexes are completely interconvertible within each series—oxalato to dichloro in excess hydrochloric acid and dichloro to oxalato in excess oxalic acid. In each case, interconversion proceeds to give a single product with more than 90% retention of configuration.

These reactions not only demonstrate the power of dissymmetric donor atoms to control the steric course of isomerization within the coordination sphere of a metal ion but also suggest that reaction pathways in which more than one donor atom is shifted are more readily accessible than has been supposed.

Acknowledgment.—The financial assistance of the donors of the Petroleum Research Fund, administered by the American Chemical Society, under Grant 1155G3, is gratefully acknowledged.

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Photoelectron Spectroscopy of Coordination Compounds. Triphenylphosphine and Its Complexes

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In the past few years photoelectron spectroscopy has been refined to the point where it can now be used to relate the chemical environment of an atom and the electron density about that atom by means of an absolute determination of electron-binding energies.[1] We wish to report the results of a study utilizing this method on some coordination compounds where back-donation may be important.

The use of photoelectron spectra to determine the effect of coordination on the electron density of a ligand is based on the fact that changes in the electron density about an atom are reflected in changes in the binding energies of the core electrons. Larger binding energies are associated with smaller electron densities.[1,2] Since coordination by simple electron pair sharing is always expected to lead to a decrease in the electron density of the ligand, one can anticipate that it should lead to larger values for the binding energies of the core electrons of the literal donor atom of the ligand. This effect will be altered where π bonding is also involved. Where π bonding involves back-donation from filled metal ion orbitals to empty ligand orbitals, the effect of π bonding is expected to counter the effect of σ bonding. In addition, in a series of compounds, there will be effects that are related to the electronegativity differences between the coordinated atoms.

In order to examine the use of photoelectron spectra in estimating the relative importance of these factors we have used such spectra to obtain the binding energies of the phosphorus 2p electrons in the compounds $(C_6H_5)_3P$, $(C_6H_5)_3P{=}O$, $Ni(P(C_6H_5)_3)_2Cl_2$, $Pd(P(C_6H_5)_3)_2Cl_2$, and $Cd(P(C_6H_5)_3)_2Cl_2$.

Experimental Section

The spectra were obtained by means of a 35-cm double-focusing electron spectrometer of the split-coil solenoidal type.[3] The majority of runs were taken at an instrumental momentum resolution of 0.05%. The spectra were calibrated using the carbon 1s line of triphenylphosphine as an internal standard. The C_{1s} binding energies and $\beta\rho$ values corresponding to the anodes used are listed in Table I.

All analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. The nickel complex was prepared by the method of Cotton, Faut, and Goodgame.[4] A similar procedure

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