Figure 3.—(a) The double layer of primary bonded atoms in the As structure. (b) The corresponding double layer of primary bonded atoms in the black phosphorus and GeSe structures.
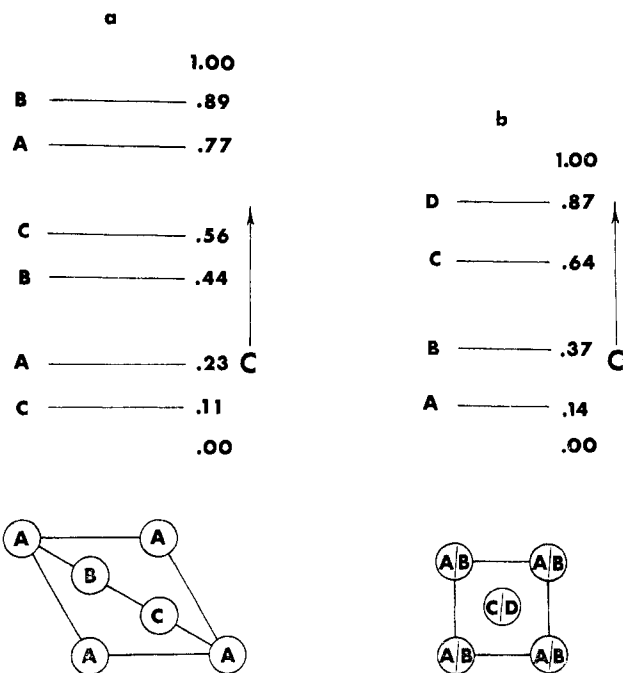

Figure 4.—Layer stacking sequences: a, arsenic structure; b, GeSe structure.

to that of arsenic and bismuth. The interatomic distances are very similar, both with respect to first neighbor coordination and the difference between first and second neighbor distances, and this is in agreement with the semimetallic character of these materials. It is not at all obvious, however, why these binary compounds have the black phosphorus rather than the arsenic structure, which is equally compatible with these first and second neighbor interactions and would permit a higher density of atomic packing.

Acknowledgment.—This research is supported by the U. S. Army Research Office (Durham) through Grant No. DA-ORD-31-124-61-G63.
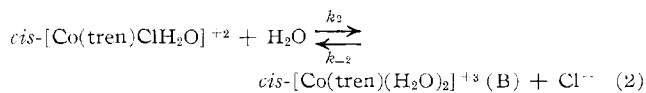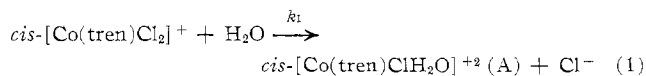
Substitution Reactions of cis-Dichloro(β,β',β''-triaminotriethylamine)cobalt(III) Complex Ion. Kinetics of Aquation of cis-Dichloro-(triaminotriethylamine)cobalt(III) Ion[1]

BY STANLEY K. MADAN,[2] WILLIAM M. REIFF,
AND JOHN C. BAILAR, JR.

The object of this study was to gain information regarding the kinetics of the aquation of cis-dichloro(triaminotriethylamine)cobalt(III) chloride, in which the steric property of the molecule is fixed, since the tertiary nitrogen atom must be *trans* to a chloro group. It has been found that the controlled configuration has a striking effect on the reaction rate under various conditions.

The aquation reaction, which has been conducted in 0.1 M acid solution, takes place in two steps, which may be written as

$$cis\text{-}[Co(tren)Cl_2]^+ + H_2O \xrightarrow{k_1}$$
$$cis\text{-}[Co(tren)ClH_2O]^{+2} (A) + Cl^- \quad (1)$$

$$cis\text{-}[Co(tren)ClH_2O]^{+2} + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}$$
$$cis\text{-}[Co(tren)(H_2O)_2]^{+3} (B) + Cl^- \quad (2)$$

The kinetic measurements made in this study may also be cited as support for the stepwise aquation, even though salts containing ion A have never been isolated. Reaction 1 proceeds at a much greater rate than reaction 2, so that no serious interference is caused

(1) This article is based upon part of a dissertation submitted by S. K. Madan in partial fulfillment of the requirements for the Ph.D. degree at the University of Illinois, 1960.
(2) Socony-Mobil Research Assistant, University of Illinois, 1956–1957.

by reaction 2 in the study of reaction 1. The diaquo species B is stable only in strongly acidic solution. It reverts to the *cis*-dichloro species after several hours in a concentrated hydrochloric acid solution. Under the conditions of the experiments reported here, it is reasonable to assume that equilibrium is not established either in reaction 1 or 2, and that, in any case, an equilibrium in reaction 1 would tend to be far toward the right.

Experimental

Preparation of Compounds.—β,β',β''-Triaminotriethylamine and the cobalt(III) complex were prepared according to the methods described by Liu.[3]

Kinetic Measurements. (a) **Spectrophotometric Method.**— The change in optical density was followed with time. The wave length chosen for the study of this reaction was the one at which a maximum absorption difference occurs between the reactant and product. For example, this maximum difference between the dichloro complex and aquochloro complex occurs at 529 mμ, which was therefore the wave length used to determine the rate of reaction 1. Measurements were made on a Cary Model 14M spectrophotometer using Pyrex cells of 1-cm. path length. The temperature was controlled to within 0.1° by circulating thermostated water through the compartment surrounding the cells. The concentration of the complex in these runs was 0.003 M.

Since optical density is proportional to concentration, the rate expression can be set up in terms of optical density. For reactions of this type, which go to completion, the initial concentration, a, is proportional to $D_\infty - D_0$ and x, the amount which has reacted, is related to $D_t - D_0$. Thus the equation

$$kt = \ln \frac{a}{a - x}$$

can be expressed as

$$kt = \ln \frac{D_\infty - D_0}{D_\infty - D_t}$$

Plots of log $(D_\infty - D_t)$ *vs.* time yield a straight line, the slope of which is $-k/2.303$. It is evident that reaction 1 is pseudo-first-order.

(b) **Conductometric Method.**—The reaction was also followed conductometrically. For these measurements, a RC-18 Industrial Instruments conductance bridge equipped with 1000-cycle and 3000-cycle signals and a cathode-ray oscillograph as the null detector was used. The conductance cell, of the standard type, was immersed in a thermostat during the course of the reaction. The concentration of the complex was approximately 0.003 M. Measurements were made at pH values of 4.0, 5.0, and 6.0, and data corresponding to those obtained with the spectrophotometric method were obtained. The reason for lowering the concentration of perchloric acid in the conductometric method was to improve the sensitivity of the method (perchloric acid having a very high specific conductance in aqueous solution) and allow comparison of the two methods.

The conductometric data were treated by the Guggenheim method to obtain the rate constant.[4] Results show a relative error of approximately 7% between the two methods.

Results and Discussion

The specific rate constant for reaction 1, k_1, found by the spectrophotometric method, is given in Table I for the conditions specified. In all cases, triplicate runs gave straight-line plots whose k_1 values agreed

(3) C. F. Liu, Doctorate Dissertation, University of Illinois, 1957.
(4) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p. 49.

within 2%. The average value of k_1 at 25° was found to be 2.96×10^{-3} sec.$^{-1}$.

TABLE I

RATES OF ACID HYDROLYSIS OF *cis*-[Co(tren)Cl₂]⁺ AT pH 1.0

Temp., °C.	Ionic strength	$k_1 \times 10^3$, sec.$^{-1}$
16.30	0.103	1.09
20.00	0.103	1.75
25.00	0.103	2.96
30.00	0.103	4.87
35.00	0.103	7.52

Table II shows the effect of various changes in conditions and of the addition of certain electrolytes on the rate of acid hydrolysis. All k_1 values represent the average of at least three or four kinetic runs. Several conclusions can be drawn from the results listed in Table II. The variation in initial concentration of complex has no effect on the rate constant.

TABLE II

RATES OF ACID HYDROLYSIS OF *cis*-[Co(tren)Cl₂]⁺ UNDER VARIOUS CONDITIONS AT 25° AND pH 1.0 (HClO₄)

Concn. of complex, $M \times 10^3$	Added electrolyte	Ionic strength	$k_1 \times 10$, sec.$^{-1}$
1.50	...	0.102	2.95
2.00	...	0.102	2.94
2.50	...	0.103	2.98
3.00	...	0.103	2.96
3.00	0.025 M Ca(ClO₄)₂	0.178	3.21
3.00	0.025 M Zn(ClO₄)₂	0.178	3.18
3.00	0.050 M NaCl	0.153	3.30
3.00	0.0125 M Na₂SO₄	0.141	3.33
3.00	0.025 M Na₂SO₄	0.178	3.59
3.00	0.050 M Na₂SO₄	0.253	3.66
3.00	0.100 M Na₂SO₄	0.403	4.09

Results of experiments containing added electrolyte can be explained by the primary salt effect, using the extended equation proposed by Davies.[5] The log ratio of the rate constants for the reaction in the presence of 0.025 M Ca(ClO₄)₂ and 0.1 M HClO₄ to that with 0.1 M HClO₄, divided by the difference in the Davies function for these ionic strengths, gives a value of 2.05 compared to a theoretical value of 2.04. This result is fortuitous, considering the range of applicability of this equation, but the agreement does indicate the operation of the primary salt effect.

Thermodynamic considerations of reaction 1, obtained from an Arrhenius plot of log k *vs.* $1/T$, are $\Delta H^* = 17.85$ kcal., $\Delta F^* = 20.95$ kcal., and $\Delta S^* = -10.40$ e.u.

It can be seen that the ions *cis*-[Co(en)₂Cl₂] and *cis*-[Co(trien)Cl₂]⁺ are not different from the *cis*-[Co(tren)Cl₂]⁺ ion in their behavior toward acid hydrolysis. This strongly suggests that these complexes undergo acid hydrolysis by similar mechanisms. The results would seem to favor an SN1 mechanism for the *cis*-dichloro(triaminotriethylamine)cobalt(III) ion. The evidence for a dissociation of the cobalt complex with *cis*-controlled configuration is interesting on the basis of at least two observations: (1) The slight increase in aquation rate which occurs when high con-

(5) C. W. Davies, *J. Chem. Soc.*, 2093 (1938).

centrations of anions known to form ion pairs are present suggests an S_N1 mechanism. (2) The relatively small negative entropy of activation found for the aquation of the *cis*-dichloro(triaminotriethylamine)-cobalt (III) ion suggests an S_N1 mechanism, since an S_N2 mechanism usually produces a rather large negative entropy.

Assuming that the cobalt complexes with controlled configuration and with uncontrolled configuration follow the same reaction path during aquation reactions, it would be gratifying to be able to explain why the one with controlled configuration shows a greater reaction rate than do *cis*-[Co(en)₂Cl₂]⁺, *cis*-[Co(trien)-Cl₂]⁺, and other dichlorocobalt ions.

Pearson and co-workers[6] have shown that the largest differences in rate are found between the completely ammoniated complexes and those which contain other bases in addition to or instead of coordinated ammonia. This suggests that the more rapid reactions of the ammonia complexes are due to the larger numbers of acidic hydrogen atoms and the absence of chelate effect in *cis*-[Co(NH₃)₄Cl₂]⁺, as compared with *cis*-[Co(en)(NH₃)₂Cl₂]⁺, *cis*-[Co(en)₂-Cl₂]⁺, and *cis*-[Co(trien)Cl₂]⁺, and in *trans*-[Co(NH₃)₄-Cl₂]⁺, as compared with *trans*-[Co(en)(NH₃)₂Cl₂]⁺ and *trans*-[Co(en)₂Cl₂]⁺. In general, the rate of aquation decreases as the amount of chelation increases. The greater rate at which *cis*-[Co(trien)Cl₂]⁺ aquates as compared with the other complexes containing organic amines is probably due simply to steric strains produced by the peculiar geometry of the complex. Rasmussen[7] has shown that in the complex [Ni(tren)-(NCS)₂], the bonds between the metal and the primary amine nitrogens are drawn back toward the tertiary nitrogen atom. This distortion would certainly put a strain on the complex, with resultant increase in reactivity. The reasonable assumption that the stereochemistry of [Co(tren)Cl₂]⁺ is similar may afford a satisfactory explanation for the increased activity of the coordinated chlorine. It does not seem to be necessary to call upon inductive or other electrical effects.[6]

(6) R. G. Pearson, C. R. Boston, and F. Basolo, *J. Phys. Chem.*, **59**, 304 (1955).

(7) S. E. Rasmussen, *Acta Chem. Scand.*, **18**, 2009 (1959).

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Magnetic Properties of Copper Benzoate[1]

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The magnetic properties of copper acetate and other copper alkylcarboxylates have been the subject of many investigations. However, little attention has been paid to the copper arylcarboxylates. Ploquin[2] reported the results of his magnetic investigations of the copper salts of several organic acids. An abnormally low moment of 1.50 B.M. was obtained for copper benzoate. Recently, the presence of a low moment for copper benzoate has been verified by two groups.[3,4] The Japanese workers[3] obtained three values for the moment depending on the method of preparation of the sample. They attributed these values to different structure types. Lewis and co-workers[5,6] have measured the magnetic susceptibilities of a number of copper salts of substituted benzoic acids. In this note we wish to report the results of our studies of the temperature dependence of the magnetic susceptibilities of samples of copper benzoate and of copper *p*-methylbenzoate. The data show that the magnetic properties are a function not only of the method of preparation but also of the history of the sample.

Experimental

Preparation of the Compounds.—The compounds, prepared by standard techniques, were characterized thoroughly; we report in Table I complete analytical data for our samples.

TABLE I

ANALYTICAL DATA

| | | Analyses | | |
	Sample	% carbon	% hydrogen	% copper
Copper benzoate	I[a]	54.28	3.44	
	II[b]	54.00	3.50	...
	III[c]	54.55	3.53	20.58
	Calcd.	54.99	3.27	20.78
Copper *p*-methylbenzoate	A[d]	56.83	4.19	19.20
	B[e]	56.28	4.49	...
	Calcd.	57.57	4.20	19.05

[a] Prepared by heating copper benzoate trihydrate at 90° under vacuum over P₂O₅. [b] Prepared by heating the trihydrate at 100° in air. [c] Prepared by heating Cu(C₆H₅CO₂)₂·C₂H₅OH at 90° in air. [d] Prepared by heating Cu(CH₃C₆H₄CO₂)₂·C₂H₅OH in air at 70° for 2 hr. [e] Prepared by heating sample A in air for 40 hr. at 90°.

X-Ray Powder Patterns.—X-Ray diffraction patterns of powdered samples were obtained using a 114.6-mm. Debye-Scherrer camera. Samples were mounted in glass capillary tubes with a diameter of 0.5 mm. and a wall thickness of 0.01 mm.

The powder pattern of anhydrous copper benzoate (sample III) consisted of lines corresponding to *d* spacings of 11.2 (9), 9.50 (10), 7.56 (2), 6.05 (7), 5.52 (4), 5.12 (5), 4.73 (8), 4.29 (1), 4.06 (6), 3.30 (4), 2.77 (3), and 2.62 (1) Å. The relative intensities which are given in parentheses were estimated visually.

Magnetic Susceptibility Determinations.—Magnetic susceptibilities were determined by the Faraday method using equipment and procedures which have been described previously.[7]

(1) This work was supported by the Advanced Research Projects Agency, the University Research Council of the University of North Carolina, and the Petroleum Research Fund, which is administered by the American Chemical Society.

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(6) J. Lewis, Y. C. Lin, L. K. Royston, and R. C. Thompson, *ibid.*, in press.

(7) W. E. Hatfield, Y. Muto, H. B. Jonassen, and J. S. Paschal, *Inorg. Chem.*, **4**, 97 (1965).