

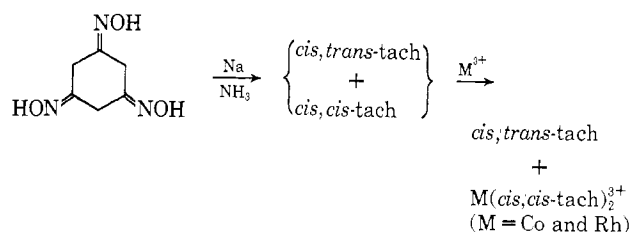
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Hindered Ligand Systems. II. The Complexes of Certain Divalent Metal Ions with *cis,cis*-1,3,5-Triaminocyclohexane

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Received November 20, 1967

It was previously demonstrated¹ that the Birch reduction of the trioxime of α -phloroglucinol yielded both stereoisomers of 1,3,5-triaminocyclohexane (*tach*) but that only *cis,cis*-*tach* was capable of forming stable bis complexes with trivalent cobalt or rhodium under the prevailing conditions



This was established by a comparison of the pmr spectrum of the mixture of isomers obtained from the Birch reduction and that due to the free ligand obtained from the decomposition of $\text{Co}(\textit{cis,cis-tach})_2^{3+}$. Since it was also shown that the isomeric ratio of the ligand obtained from the reduction was approximately 1:1, the syntheses of the complex ions can be viewed as competition experiments in which only the *cis,cis* isomer effectively competes for the metal ion. This feature is apparently not limited to systems containing trivalent metal ions but functions equally well with certain divalent ions. This publication describes the properties of the new complexes, as well as pointing to a convenient method for preparing *cis,cis*-*tach* in excellent isomeric purity.

Experimental Section

Preparation of Bis Complexes.—An aqueous solution (5 ml) containing the hydrated metal nitrate (0.001 mol) was added slowly to a solution (10 ml) containing 0.51 g (0.004 mol) of the

in air. Yields were nearly quantitative in all cases. In the case of the Co(II) complex, the entire operation was performed under nitrogen but the dry crystals appeared to be stable in air. Also, in the preparation of the Cd(II) complex, it was necessary to buffer the amine solution with 2 drops of glacial acetic acid in order to prevent the formation of some $\text{Cd}(\text{OH})_2$. Only the Ni(II) compound could survive recrystallization. The analytical results and colors of the compounds are given in Table I. The corresponding perchlorates can also be prepared in this manner. Two examples are also given in the table.

Ni(*cis,cis-tach*)(NO₃)₂·3H₂O.—When equimolar quantities of $\text{Ni}(\textit{cis,cis-tach})_2(\text{NO}_3)_2$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were heated in a small quantity of water, the pink crystals soon dissolved to give a deep blue solution. The solvent was removed on a steam bath, and the blue material was taken up in a minimum quantity of hot 95% ethyl alcohol. After filtering, the solution was allowed to cool. The resulting blue crystals were filtered, washed with alcohol, and dried in air. The analytical results were included in Table I. This reaction is apparently unique with the Ni(II) complex. Attempts to utilize similar reactions with other metal ions were not successful.

Decomposition of Ni(*cis,cis-tach*)₂(NO₃)₂.—When crystals of this compound are covered with 12 M HCl, solution occurs with the concurrent deposition of white crystals of *cis,cis-tach*·3HCl·H₂O. The pmr spectrum of this compound was identical with that previously obtained.¹

Magnetic Measurements.—The Faraday apparatus was previously described.² The instrument was calibrated using $\text{Hg}[\text{Co}(\text{NCS})_4]$. Pascal's constants³ were used to estimate diamagnetic corrections. Some of the results are included in Table I.

X-Ray Powder Patterns.—Powder patterns were obtained using vanadium-filtered chromium K α radiation. The results, given in Table II, clearly indicate that all compounds are isomorphous.

Discussion of Results

The magnetic moments of the paramagnetic bis complexes, as shown in Table I, clearly indicate their octahedral nature. This is particularly true in the case of the $\text{Co}(\textit{cis,cis-tach})_2^{2+}$ ion, since magnetic moments between 5.0 and 5.3 BM are generally given for octahedral complexes containing that metal ion. Furthermore, the crystallographic data in Table II indicate that the Zn(II) and Cd(II) compounds are isomorphous and presumably isostructural with the paramagnetic compounds. Since the decomposition of the Ni(II) compound led to the isolation of isomerically pure *cis,cis-tach*·3HCl·H₂O, the presence of the *cis,cis* isomer of the ligand in all of the complexes is assured.

TABLE I
ANALYTICAL RESULTS AND PHYSICAL PROPERTIES

Compound	% C		% H		% N		Color	μ_{eff} (300°K)
	Calcd	Found	Calcd	Found	Calcd	Found		
$\text{Co}(\textit{cis,cis-tach})_2(\text{NO}_3)_2$	32.65	32.96	6.85	6.74	25.40	25.33	Buff	5.05
$\text{Ni}(\textit{cis,cis-tach})_2(\text{NO}_3)_2$	32.67	32.92	6.86	6.87	25.41	25.29	Pink	3.17
$\text{Zn}(\textit{cis,cis-tach})_2(\text{NO}_3)_2$	32.18	32.30	6.75	6.89	25.04	25.17	White	...
$\text{Cd}(\textit{cis,cis-tach})_2(\text{NO}_3)_2$	29.14	28.99	6.11	6.36	22.67	22.75	White	...
$\text{Co}(\textit{cis,cis-tach})_2(\text{ClO}_4)_2$	27.91	27.98	5.86	5.91	16.28	16.29	Buff	5.10
$\text{Ni}(\textit{cis,cis-tach})_2(\text{ClO}_4)_2$	27.93	28.31	5.86	5.90	16.29	16.26	Pink	3.17
$\text{Ni}(\textit{cis,cis-tach})_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	19.69	19.84	5.78	5.86	19.14	18.87	Blue	3.12

mixture of *tach* isomers, which was prepared as previously described.¹ Crystallization generally occurred during the addition. The mixture was then stirred for 1 hr, whereupon the crystals were removed by filtration, washed with water, and dried

At this point the possibility of molecular and electronic distortions within the complex ion is of interest

(2) R. Saillant, J. L. Hayden, and R. A. D. Wentworth, *Inorg. Chem.*, **6**, 1497 (1967).

(3) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, p 415.

(1) R. A. D. Wentworth and J. J. Felten, *J. Am. Chem. Soc.*, **90**, 621 (1968).

TABLE II

X-RAY DIFFRACTION DATA FOR $M(\text{cis},\text{cis-tach})(\text{NO}_3)_2^a$			
M = Co	M = Ni	M = Zn	M = Cd
8.68	8.63	8.72	8.99
6.74	6.77	6.74	6.80
5.12	5.12	5.13	5.12
4.35	4.34	4.35	4.37
2.86	2.86	2.87	2.87

^a d_{hkl} values for five strongest lines.

because the ligand would appear to be capable of inducing both. Since the ionic radii of the Zn(II) and Cd(II) ions are about 0.7 and 1.0 Å, respectively, it is clear that the size of the metal ion, at least within these limits, will not alone be an important feature in the formation of these adamantane-like complexes. The lower limit of the ionic radius must extend to at least 0.6 Å, the approximate radius of Co(III), but even an approximate upper limit has not yet been determined. Obviously, however, the triaxial conformation of the ligand can accommodate metal ions of diverse radii. Necessarily, if this is the case, distortions may be introduced either into the MN_6 octahedron or into the ligand framework. Since the infrared spectra of these complexes are virtually identical between 700 and 3000 cm^{-1} , it seems unlikely that the latter are significant. At present, the possibility of atomic distortions within the MN_6 octahedron remains unanswered, but electronic distortions within the paramagnetic complex ions have received some attention. The reflectance spectra of the chromophoric compounds are given in Table III. The ligand field parameters, which compare reasonably well to those of the corresponding $M(\text{en})_3^{2+}$ ions, would appear to rule out unusually large electronic distortions.

TABLE III

REFLECTANCE SPECTRA OF $M(\text{cis},\text{cis-tach})_2(\text{NO}_3)_2$

M	$\text{cm}^{-1} \times 10^{-3}$	Assignment	Dq, cm^{-1}	B, cm^{-1}
Co	10.4	${}^4\text{T}_1(\text{F}) \rightarrow {}^4\text{T}_2$	1170	800
	21.1	${}^4\text{T}_1(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$		
Ni	11.7	${}^3\text{A}_2 \rightarrow {}^3\text{T}_2$	1170	930
	18.7	${}^3\text{A}_2 \rightarrow {}^3\text{T}_1(\text{F})$		

Magnetic susceptibility measurements can also provide information about electronic distortions. In certain instances, distortions within excited states may be inferred from the measurement of the zero-field splitting. Such a case is provided with the salts of the $\text{Ni}(\text{cis},\text{cis-tach})_2^{2+}$ ion. The temperature dependence of the reciprocal susceptibility of $\text{Ni}(\text{cis},\text{cis-tach})_2(\text{NO}_3)_2$ is shown in Figure 1. A least-squares analysis of the data yielded the Curie-Weiss expression $\chi_M = 1.27/(T + 3)$. The Weiss constant could be at least partially due to lattice effects. However, as shown in the figure, the reciprocal susceptibility of $\text{Ni}(\text{cis},\text{cis-tach})_2(\text{ClO}_4)_2$ closely follows that of the nitrate. Since their crystal structures are probably not similar, magnetic dilution appears likely in each case. If it is assumed that only axial distortions are present (trigonal in this case), the Weiss constant may be related to

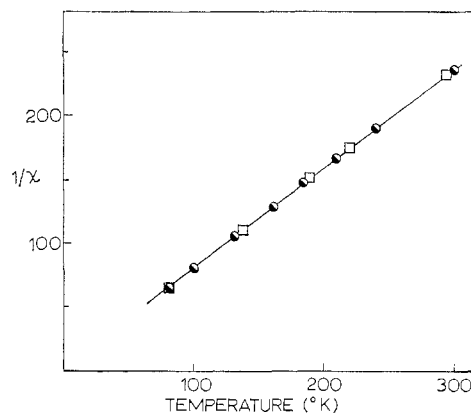


Figure 1.—Experimental variation of the reciprocal susceptibility with temperature: ●, $\text{Ni}(\text{cis},\text{cis-tach})_2(\text{NO}_3)_2$; □, $\text{Ni}(\text{cis},\text{cis-tach})_2(\text{ClO}_4)_2$.

the splitting⁴ of the ${}^3\text{T}_{2g}$ state. An approximate expression for the susceptibility⁵ is

$$\bar{\chi}_M = \frac{2N\beta^2}{3k} \frac{\bar{g}^2}{T + (\delta/3k)} + N(\alpha)$$

wherein the average values of χ_M and g^2 are required owing to the anisotropic system, and δ/k is the zero-field splitting. Taking $N(\alpha)$ as $8N\beta^2/10Dq = 178 \times 10^{-6}$ cgs unit and assuming $\delta/k = 0$, the data agree reasonably with susceptibilities calculated from the expression

$$\bar{\chi}_M = \frac{1.21}{T} + 178 \times 10^{-6}$$

Since the zero-field splitting is directly proportional to the splitting of the first excited state, any electronic distortions must be very small. However, this result can only be considered an estimate in view of the experimental uncertainties and the approximate nature of the calculation. Of course, exact measurements of the zero-field splitting are possible through electron spin resonance.

The susceptibility of the Co(II) complex should provide a far more stringent test of the magnitude of electronic distortions since the octahedral ground state (${}^4\text{T}_{1g}$) is capable of first-order distortions due to low-symmetry components of the ligand field. With no distortion and ignoring electron delocalization, the expression for the square of the magnetic moment has been given⁷ by Figgis and Lewis. The parameter A from their expression can be obtained from spectroscopic measurements and for the complex in question is about 1.4. Using this value and $\lambda = -170 \text{ cm}^{-1}$, the calculated magnetic moment at 300°K is 5.08 BM, in close agreement with the experimental values given in Table I. Thus, significant ligand field distortions are probably not present within the ground state.

(4) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(5) This expression is identical with the result obtained by Carlin⁶ when the exponential terms in his expression are expanded, first order terms retained, and the expression recast in Curie-Weiss form.

(6) R. L. Carlin, *J. Chem. Educ.*, **41**, 521 (1966).

(7) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 66 (1964).

Other Reactions.—In addition to the reactions which lead exclusively to the bis complexes, there are two other reactions which are worthy of note. The first is the equilibration of $\text{Ni}(\text{cis},\text{cis}\text{-tach})_2^{2+}$ with an equivalent quantity of $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ to give, at least in solution, $\text{Ni}(\text{cis},\text{cis}\text{-tach})(\text{H}_2\text{O})_5^{2+}$. When the preparations of the Zn(II) and Cd(II) compounds were attempted, considerable quantities of the insoluble metal hydroxide were obtained. No attempt was made to prepare the Co(II) compound because of the ease of oxidation. The second reaction, which has been of considerable importance within this laboratory, is the acid decomposition of $\text{Ni}(\text{cis},\text{cis}\text{-tach})_2^{2+}$. From this reaction isomerically pure ligand can readily be obtained. Earlier,¹ the decomposition of $\text{Co}(\text{cis},\text{cis}\text{-tach})_2^{3+}$ in strong base was described. Although this reaction serves the same purpose, the kinetic stability of the Co(III) complex precludes utilization of this reaction as a preparative method. The lability of the Ni(II) complex in strong acid, however, facilitates the isolation of the pure ligand in large quantities, and additional studies which require the ligand uncontaminated with the *cis,trans* isomer have been possible. Some of these will be described in a subsequent publication.

Acknowledgment.—This research was supported by the National Science Foundation under Grant No. GP-5764.

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Anation of $\text{cis-Co}(\text{en})_2\text{NO}_2\text{dmsO}^{2+}$ Ion in Dimethyl Sulfoxide: Dissociative Interchange¹

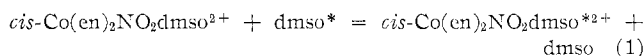
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Received November 22, 1967

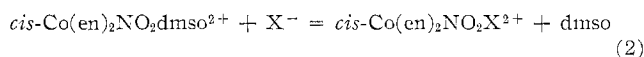
Substantial evidence has accumulated to implicate bond breaking (dissociation) as the mode of activation in substitution reactions of octahedral complexes of cobalt(III).³ However, several experiments⁴⁻⁶ document the absence of a kinetically detectable five-coordinate intermediate in many cases. Of course, a dissociative mode of activation need not be accompanied by an intermediate. The point along the reaction coordinate with negligible bonding to either entering or leaving ligand may be merely the transition state. Such a situation has been termed dissociative inter-

change.⁶⁻⁸ The entering group will appear in the rate law for dissociative interchange because it is a stoichiometric component of the transition state. However, all entering groups should react at the *same rate* if their encounters⁹ with the substrate site are equally probable. In ion pairs between a cationic complex and an anionic entering group, different anions should have very similar probabilities for encounter with the reactive site on the substrate complex. However, the complex is simultaneously in encounter with several solvent molecules so that it is more probable that the crucial site on the complex is in encounter with a solvent molecule than an anion. Thus, we would expect the first-order rate constants for formation of inner-sphere complexes from ion pairs to be similar for all anions (dissociative mode of activation) but to lie below the rate constant for solvent exchange (since the probability of encounter with the solvent is higher).

The relationship between solvent-exchange rate and anation rate in ion pairs may distinguish dissociative interchange (I_d^{10}) from the conventional dissociative pathway *via* an intermediate of reduced coordination number (D^{10}). Recently, Watts and Lantzke¹¹ reported an elegant nmr experiment using a deuterium tracer to obtain the solvent-exchange rates of some dimethyl sulfoxide (dmsO) complexes dissolved in dimethyl sulfoxide. For example, they report a rate constant of $3.07 \pm 0.07 \times 10^{-4} \text{ sec}^{-1}$ at 35° for the reaction



where the asterisk indicates labeled dmsO and en is ethylenediamine. Tobe, Watts, and their coworkers have also shown that ion association between Co(III) complex cations and simple anions is quite pronounced at *low* electrolyte concentrations in dimethyl sulfoxide.^{12,13} In this note, we report rates of the reactions



(where $\text{X}^- = \text{Cl}^-, \text{NO}_2^-,$ and SCN^-) in dimethyl sulfoxide at 35.0° and at a constant ionic strength of $0.050 M$ maintained with $(\text{C}_6\text{H}_5)_4\text{AsClO}_4$. As anion concentrations are increased, the pseudo-first-order rate constants obtained approach a limit in two of the cases. This limiting rate is clearly associated with saturation of the equilibrium forming the ion pairs $\text{cis-Co}(\text{en})_2\text{NO}_2\text{dmsO}^{2+}, \text{X}^-$. The rate of formation of $\text{cis-Co}(\text{en})_2\text{NO}_2\text{X}^{2+}$ from these ion pairs is the limiting rate. It may be compared to the solvent-exchange rate.

(1) We gratefully acknowledge support from the donors of the Petroleum Research Fund administered by the American Chemical Society.

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(3) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin Inc., New York, N. Y., 1966, Chapter 3.

(4) R. G. Pearson and J. W. Moore, *Inorg. Chem.*, **3**, 1334 (1964).

(5) N. V. Duffy and J. E. Earley, *J. Am. Chem. Soc.*, **89**, 272 (1967).

(6) B. Bosnich, J. Ferguson, and M. L. Tobe, *J. Chem. Soc., A*, 1636 (1966).

(7) C. H. Langford and W. R. Muir, *J. Am. Chem. Soc.*, **89**, 3141 (1967).

(8) R. G. Pearson and P. Ellgen, *Inorg. Chem.*, **6**, 1379 (1967).

(9) The term "encounter" is used in the limited sense of the theory of fast reactions in the liquid state to refer to partners trapped together by what is sometimes called the "solvent cage."

(10) See ref 3, Chapter 1.

(11) D. W. Watts and I. Lantzke, *J. Am. Chem. Soc.*, **89**, 816 (1967).

(12) M. L. Tobe and D. W. Watts, *J. Chem. Soc.*, 2991 (1964).

(13) L. F. Chin, W. A. Millen, and D. W. Watts, *Australian J. Chem.*, **18**, 453 (1965).