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Complexes of Triethylphosphine and Triethylarsine with the Halides of Cobalt(II) and Zinc[1]

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Calcium chloride does not react with triethylphosphine (nor presumably with triethylarsine), but cobalt(II) and zinc halides give complexes containing two moles of base per mole of salt. Of these, the compound $CoCl_2\cdot 2P(C_2H_5)_3$ has long been known.[2] All the compounds have negligible dissociation pressures at 25°, but one-half the base is lost from the $CoX_2\cdot 2As(C_2H_5)_3$ compounds on long standing or on heating at 100° *in vacuo* for 1 day. X-Ray diffraction patterns of the products prove that true 1:1 complexes are formed. The magnetic moments and spectra of the cobalt complexes are interpreted as indicating tetrahedral coördination. A preliminary value of the magnetic moment of $CoCl_2\cdot 2P(C_2H_5)_3$ of Jensen cited by Nyholm[3] is found to be in error. The tertiary phosphine and arsine complexes are compared with the previously reported[4] triethylamine complexes. A vapor pressure–temperature relation for triethylarsine is presented.

Introduction

It has been shown[4] that triethylamine does not react with anhydrous calcium or zinc halides, and that it gives only 1:1 complexes with the cobalt(II) halides. These 1:1 complexes are thought to be halogen-bridged dimers or polymers, since the magnetic moments and spectra indicate tetrahedrally coördinated cobalt.

The coördinating abilities of triethylphosphine and triethylarsine have now been studied, using the reference acids calcium, cobalt(II), and zinc ions as examples of the 8, incomplete, and 18-electron configurations.

A great number of tertiary alkylphosphine and arsine metal complexes is known. None of these involves alkaline earth metal ions. Quite a few cadmium and mercury(II) complexes of this type are known, but apparently the zinc systems have not been studied.[4a] Of the many transition metal complexes which have been prepared, the compound $CoCl_2\cdot 2P(C_2H_5)_3$ prepared by Jensen[2] is of particular relevance to this work.

One of the most interesting things to be observed in a survey of the known compounds is the variation in the stoichiometry of coördination. Complexes containing 0.5, 0.67, 1, 1.5, and 2 moles of base per mole of salt are most common. It is not clear that all these represent successive steps of reversible dissociation in passing from the highest complex to the simple salt. Divalent metal ion coördination complexes of the 2:1 and 1:1 types in these systems are commonly monomers and dimers, respectively, as shown in a number of cases by X-ray diffraction studies of the crystals and molecular weight determinations using benzene solutions. Representatives of other coördination stoichiometries are mostly of unknown structure.

The following triethylphosphine complexes and triethylarsine complexes of Group II and divalent first transition series metal halides have been reported: $CdBr_2\cdot 1,2P(C_2H_5)_3$[5]; $CdI_2\cdot 1,2P(C_2H_5)_3$[5]; $HgCl_2\cdot 0.5,1P(C_2H_5)_3$[5,6]; $HgBr_2\cdot 0.5,0.67,1P(C_2H_5)_3$[5]; $HgI_2\cdot 0.67,1,2P(C_2H_5)_3$[5,7]; $CrCl_2\cdot 1,2P(C_2H_5)_3$[8]; $CrBr_2\cdot 1,2P(C_2H_5)_3$[8]; $CoCl_2\cdot 2P(C_2H_5)_3$[2,3,9]; $NiCl_2\cdot 2P(C_2H_5)_3$[10]; $NiBr_2\cdot 2P(C_2H_5)_3$[10,11]; $NiI_2\cdot 2P(C_2H_5)_3$[10]; $CdBr_2\cdot As(C_2H_5)_3$[5]; $CdI_2\cdot 1,2As(C_2H_5)_3$[5]; $HgCl_2\cdot 0.5,1As(C_2H_5)_3$[5,12]; $HgI_2\cdot 0.67,1,1.5As(C_2H_5)_3$[5]; $NiI_2\cdot 2As(C_2H_5)_3$.[10]

In this work, the coördination reactions were observed in the course of an isothermal study of

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(1) Abstracted from the Dissertation of W. E. Hatfield, submitted to the Graduate College of the University of Arizona in partial fulfillment of the requirements for the Ph.D. degree, 1962.

(2) K. A. Jensen, *Z. anorg. allgem. Chem.*, **229**, 282 (1936).

(3) R. S. Nyholm, *J. Chem. Soc.*, 2073 (1950).

(4) W. E. Hatfield and J. T. Yoke, *Inorg. Chem.*, **1**, 463 (1962).

(4a) NOTED ADDED IN PROOF.—The compound $ZnCl_2\cdot 2P(C_2H_5)_3$ has been prepared, and reported to have an electric moment of 7.6 D.: M. J. Schmelz, M. A. G. Hill, and C. Curran, *J. Phys. Chem.*, **65**, 1273 (1961).

(5) R. C. Evans, F. G. Mann, H. S. Peiser, and D. Purdie, *J. Chem. Soc.*, 1209 (1940).

(6) J. A. C. Allison and F. G. Mann, *ibid.*, 2915 (1949).

(7) R. C. Cass, G. E. Coates, and R. G. Hayter, *ibid.*, 4007 (1955).

(8) K. Issleib and H. O. Frölich, *Z. anorg. allgem. Chem.*, **298**, 84 (1959).

(9) J. T. Yoke, Dissertation, University of Michigan, 1954.

(10) K. A. Jensen, *Z. anorg. allgem. Chem.*, **229**, 265 (1936).

(11) G. Giacometti, V. Scatturin, and A. Turco, *Gazz. chim. ital.*, **88**, 434 (1958); V. Scatturin and A. Turco, *J. Inorg. Nucl. Chem.*, **8**, 447 (1958).

(12) E. Gryszkiewicz-Trochimowski, M. Buczwinski, and J. Kwapiszewski, *Roczinki Chem.*, **8**, 423 (1928); *Chem. Abstr.*, **23**, 1614 (1929); F. Challenger and L. Ellis, *J. Chem. Soc.*, 396 (1935).

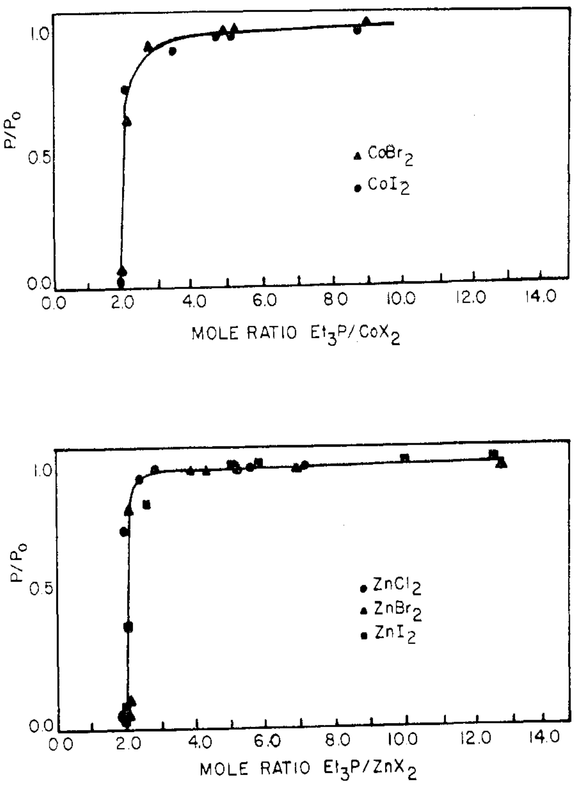

Fig. 1.—25.0° isotherms, triethylphosphine with cobalt(II) and zinc halides.

the pressure as a function of composition in the base–salt systems. An excess of the pure phosphine or arsine was condensed onto a sample of each anhydrous metal halide in a tared tube attached to a high vacuum line. Portions of the volatile base then were removed by distillation in the vacuum system. The pressures were measured at 25.0°.

Results

Calcium chloride and an excess of triethylphosphine were equilibrated overnight. The base then was quickly and quantitatively recovered by distillation in the vacuum system, indicating that there was no complex formation. Since triethylamine also failed to react with calcium chloride,[4] it was assumed that there was no point in studying the $CaCl_2$–$(C_2H_5)_3As$ system.

The 25° pressure–composition phase diagrams for the triethylphosphine and triethylarsine cobalt(II) and zinc halide systems are shown in Fig. 1 and 2. It is clear that coördination compounds of the type $MX_2 \cdot 2(lig)$ are formed in each case. The cobalt(II) chloride–triethylphosphine system had been studied previously[9,13] under identical conditions and gave results just like those reported here for the corresponding bromide and iodide systems. No complexes higher than 2:1 are formed in these systems, and the dissociation pressures of these complexes were negligibly small so that reversible dissociation of the 2:1 compounds into lower complexes or the simple salts could not be observed.

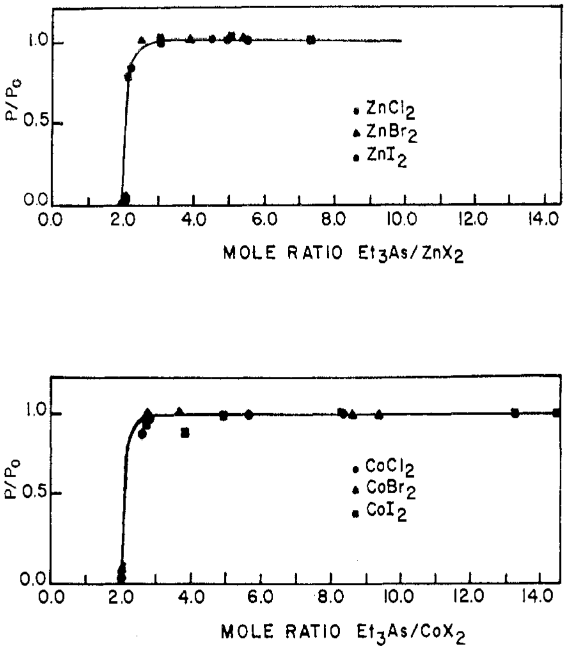

Fig. 2.—25.0° isotherms, triethylarsine with cobalt(II) and zinc halides.

When the trap containing a complex at room temperature was opened directly to the vacuum line pumping system for several hours, only small amounts of triethylphosphine or -arsine were lost. The dihalobis-(triethylarsine)-cobalt(II) complexes showed less stability than the other compounds under these conditions. When they were heated at 100° for one day, one-half of the arsine was lost, giving compounds of the type $CoX_2 \cdot As(C_2H_5)_3$.

A preliminary pressure-composition study also indicated that 1:1 complexes were formed in the cobalt(II)–triethylarsine systems. In this preliminary experiment less time was allowed for equilibration and the reaction mixture was not stirred. The vapor pressure of triethylarsine was observed throughout the composition range above a mole ratio of $(C_2H_5)_3As:CoX_2 = 1.0$, and just at and below this mole ratio value the pressure was negligible. In subsequent work, with stirring and with time periods up to one day at each point allowed for attainment of equilibrium, the data of Fig. 2 were obtained.

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(13) J. T. Yoke, G. Kodama, and R. W. Parry, unpublished work.

Still another observation indicates that 1:1 compounds are intermediate between the simple salts and the 2:1 complexes in the cobalt(II)–triethylarsine systems. Newly prepared 2:1 compounds gave satisfactory analytical results, but after storage for 6 months in screw-cap bottles in a vacuum desiccator the analyses of these compounds indicated that one-half of the triethylarsine had been lost. Analytical data for all the compounds are given in Table I.

TABLE I

ANALYTICAL DATA

	Mole ratio base:salt	% Halide	
	Found	Found	Calcd.
$CoBr_2 \cdot 2P(C_2H_5)_3$	1.94	36.1	35.6
$CoI_2 \cdot 2P(C_2H_5)_3$	1.96	46.6	46.3
$CoCl_2 \cdot 2As(C_2H_5)_3$	2.00	16.1	15.7
$CoBr_2 \cdot 2As(C_2H_5)_3$	2.00	...	...
$CoI_2 \cdot 2As(C_2H_5)_3$	1.98	38.7	39.3
$CoCl_2 \cdot As(C_2H_5)_3$	0.95[a]	24.4[b]	24.3
$CoBr_2 \cdot As(C_2H_5)_3$	...	41.2[b]	41.9
$CoI_2 \cdot As(C_2H_5)_3$	...	53.8[b]	53.5
$ZnCl_2 \cdot 2P(C_2H_5)_3$	1.92	18.9	19.0
$ZnBr_2 \cdot 2P(C_2H_5)_3$	1.98	34.6	34.2
$ZnI_2 \cdot 2P(C_2H_5)_2$	1.99	44.9	45.7
$ZnCl_2 \cdot 2As(C_2H_5)_3$	1.95	15.2	15.4
$ZnBr_2 \cdot 2As(C_2H_5)_3$	2.05	28.4	29.1
$ZnI_2 \cdot 2As(C_2H_5)_3$	1.99	39.9	39.5

[a] Obtained from the 2:1 complex by heating at 100° for 1 day. [b] Obtained from the 2:1 complex after storage for 6 months.

To ensure that the 1:1 cobalt–arsine complexes obtained in the three different ways were individual compounds and not partly hydrated cobalt halides or 50:50 mixtures of CoX_2 and $CoX_2 \cdot 2As(C_2H_5)_3$ obtained by coincidence, some X-ray diffraction powder patterns were obtained. The results are given in Table II. In the first two columns, $CoBr_2 \cdot As(C_2H_5)_3$ (a) prepared from the components using a short time of reaction is compared with $CoBr_2 \cdot As(C_2H_5)_3$ (b) obtained as the decomposition product of $CoBr_2 \cdot 2As(C_2H_5)_3$ after storage for 6 months in a vacuum desiccator. There is good agreement in d-spacings and relative intensities. In the third and fourth columns of Table II, $CoCl_2 \cdot As(C_2H_5)_3$ (prepared by heating $CoCl_2 \cdot 2As(C_2H_5)_3$ at 100° for 1 day *in vacuo*) is compared with $CoCl_2 \cdot 2As(C_2H_5)_3$. It is clear that the 1:1 complex is not simply a mixture containing the 2:1 complex.

The room temperature magnetic susceptibilities of some of the cobalt complexes were determined by the Gouy technique, and values of the magnetic moments, calculated as described previously,[4] are given in Table III.

The reflectance spectra in the visible region of some of the cobalt complexes were obtained as described previously[4] and are given in Fig. 3–5. Values of λ_{cog}, the wave lengths of the centers of gravity of the absorption bands, estimated graphically from the spectra, are given in Table III.

Experimental

The preparation of the anhydrous metal halides and the experimental technique used in the isothermal pressure–composition studies, the magnetic susceptibility determinations, and the reflectance spectra measurements have been described previously.[4]

Triethylphosphine was prepared by the Grignard reaction in a nitrogen atmosphere using Reagent Grade magnesium, phosphorus trichloride, ethyl iodide, and diethyl ether according to the method of Hibbert as modified by Mann and Wells.[14] The nitrogen was purified as described previously.[4] The product was collected as the silver iodide complex, which was dried over KOH and transferred to a bulb attached to the vacuum line. The free base was obtained by warming the silver iodide complex *in vacuo*. The triethylphosphine was purified by fractional distillation in the vacuum system until its vapor pressure over a range of temperatures agreed with the literature[15] values (14.1 mm. at 25°; 3.8 mm. at 0°).

Triethylarsine was prepared similarly, using Reagent Grade arsenic trichloride and ethyl bromide. It was collected as the silver iodide complex, which was recrystallized from acetone. The free base was liberated as above, and fractionated in the vacuum system to give a middle portion which was tensiometrically homogeneous. The vapor pressures were determined carefully at three temperatures and these data, combined with two values from the literature, are given in Table IV and can be approximated by the equation

$$\log P = -2070/T + 7.876$$

Dichlorobis-(triethylphosphine)-cobalt(II) was prepared by interaction of anhydrous cobalt(II) chloride with an excess of triethylphosphine in a trap on the vacuum line, followed by removal of the excess base *in vacuo*. *Anal.* Mole ratio $(C_2H_5)_3P:CoCl_2$ found 2.00; %Cl found 19.2, calcd. 19.4.

Analytical.—Halide analyses were by the Volhard method. Values for the mole ratio base:salt were determined by weighing the tared reaction tube at the point at which the pressure became negligibly small, as described previously.[4]

X-Ray Diffraction Powder Patterns.—A Phillips X-ray generator equipped with a diffractometer and scintillation counter were used, with copper Kα radiation filtered

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(14) H. Hibbert, *Ber.*, **39**, 160 (1906); F. G. Mann and A. F. Wells, *J. Chem. Soc.*, 702 (1938).

(15) H. W. Thompson and J. W. Linnett, *Trans. Faraday Soc.* **32**, 681 (1936).

TABLE II

X-RAY DIFFRACTION POWDER PATTERNS FOR TRIETHYLARSINE COBALT(II) COMPLEXES

$CoBr_2 \cdot As(C_2H_5)_3$ (a)		$CoBr_2 \cdot As(C_2H_5)_3$ (b)		$CoCl_2 \cdot As(C_2H_5)_3$		$CoCl_2 \cdot 2As(C_2H_5)_3$	
d	Intensity	*d*	Intensity	*d*	Intensity	*d*	Intensity
2.04	14	2.04	13	2.17	13	2.14	25
2.10	18	2.06	24	2.36	20	2.29	30
2.22	26	2.23	26	2.63	8	2.37	45
2.39	14	2.38	8	2.71	13	2.65	20
2.42	15	2.43	13	2.82	13	2.71	55
2.61	15	...	...	2.99	13	2.85	25
2.81	18	2.82	24	3.18	90	4.27	60
2.88	18	2.90	18	3.34	38	5.50	100
3.00	32	3.02	34	3.69	23		
3.14	15	3.16	13	3.83	23		
3.23	85	3.25	74	3.93	43		
3.34	27	3.38	13	4.19	33		
3.43	32	3.45	29	4.29	38		
3.59	11	...	...	5.99	43		
3.65	12	...	...	6.42	43		
3.72	18	3.75	21	7.20	100		
3.87	14	3.88	16				
4.04	51	4.06	58				
4.21	29	4.23	37				
4.31	100	4.33	100				
...	...	4.48	16				
...	...	4.53	13				
4.76	20	4.72	18				
4.98	18	5.04	16				
5.34	20	5.40	18				
6.03	14	6.07	18				
6.42	80	6.51	66				

TABLE III

MAGNETIC AND SPECTRAL DATA FOR COBALT(II) COMPLEXES

	μ_{eff}, B.M.	λ_{cog} mμ
$CoCl_2 \cdot 2P(C_2H_5)_3$	4.39	650
$CoBr_2 \cdot 2P(C_2H_5)_3$	4.76	660
$CoI_2 \cdot 2P(C_2H_5)_3$	4.74	650
$CoCl_2 \cdot 2As(C_2H_5)_3$	4.75	670
$CoCl_2 \cdot As(C_2H_5)_3$	4.70	620
$CoBr_2 \cdot As(C_2H_5)_3$	...	625
$CoI_2 \cdot As(C_2H_5)_3$	...	660

through nickel foil. Values for *d*-spacings for the angle 2θ were taken from a Department of the Interior compilation.[16]

Discussion

It is an oversimplification to take the number of molecules of base coördinated per metal ion in the stable complexes as a measure of the relative coördinating abilities of the Lewis acids and bases. The enthalpy terms depend not only on coördinate bond energies, but also on the differences in lattice energy of the simple and complex salts. The entropy terms likewise are compounded from

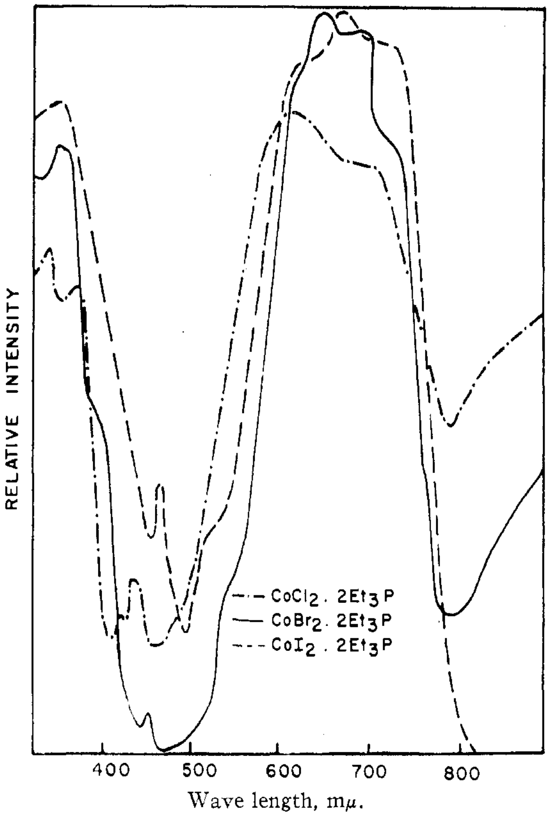

Fig. 3.—Reflectance spectra of dihalobis-(triethylphosphine)-cobalt(II) complexes.

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[16] G. Switzer, J. M. Axelrod, M. L. Lindberg, and E. S. Larsen, "Tables of *d* Spacings for Angle 2θ," U. S. Department of the Interior Geological Survey Circular 29, Washington, D. C., 1948.

several factors. Nevertheless, the stoichiometries of coördination do suggest the reasonable series Ca < Zn < Co(II) and R_3N < R_3As <R_3P. These series are based on the observations that: (a) only zinc and cobalt(II) halides react with the tertiary arsine and phosphine, (b) only the cobalt(II) halides react with triethylamine, (c) cobalt forms only 1:1 compounds with R_3N, only 2:1 compounds with R_3P, and both 1:1 and 2:1 compounds with R_3As.

TABLE IV

VAPOR PRESSURE OF TRIETHYLARSINE[a]

T, °K.	P, mm. Obsd.	P, mm. Calcd.
273.2	2.0	2.0
298.2	8.9	8.6
308.2	14.0	14.5
309.7–310.2	15.5[b]	15.8
413	736[c]	733

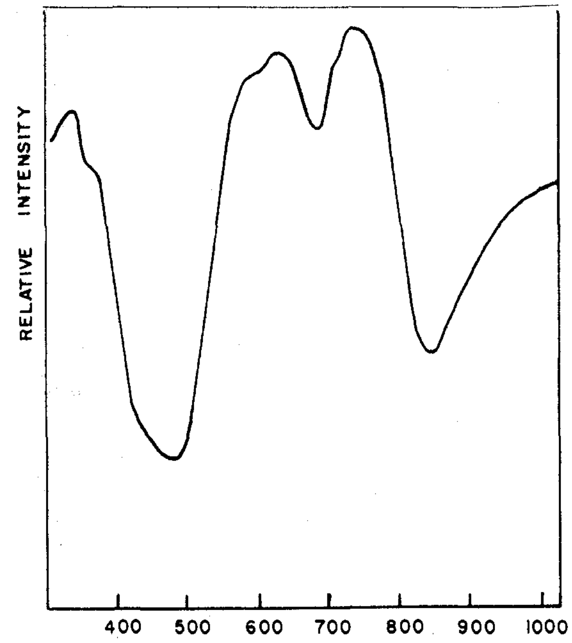
[a] ΔH_{vap} (mean) = 9.5 kcal./mole; b.p. (extrapolated) 141°; Trouton constant 23 cal./mole-deg. [b] K. I. Kuz'min and G. Kamai, *Sb. Statei Obshch. Khim., Akad. Nauk SSSR*, **1**, 223 (1953); *Chem. Abstr.*, **49**, 841 (1955). [c] H. Landolt, *Ann.*, **89**, 301 (1854).

Likewise, it is dangerous to take the results of displacement reactions involving a change of state as measures of relative coördinate bond strength. That a stronger but more volatile Lewis base may be displaced by a weaker but less volatile Lewis base from a coördination compound in a condensed phase has been demonstrated by Coates[17] in a study of the trimethyl gallium–dimethyl ether–trimethylarsine system. Thus, the known reaction[9]

$$CoCl_2\cdot N(C_2H_5)_3(c) + 2P(C_2H_5)_3(l,\ g) \longrightarrow CoCl_2\cdot 2P(C_2H_5)_3(c) + N(C_2H_5)_3(l,\ g)$$

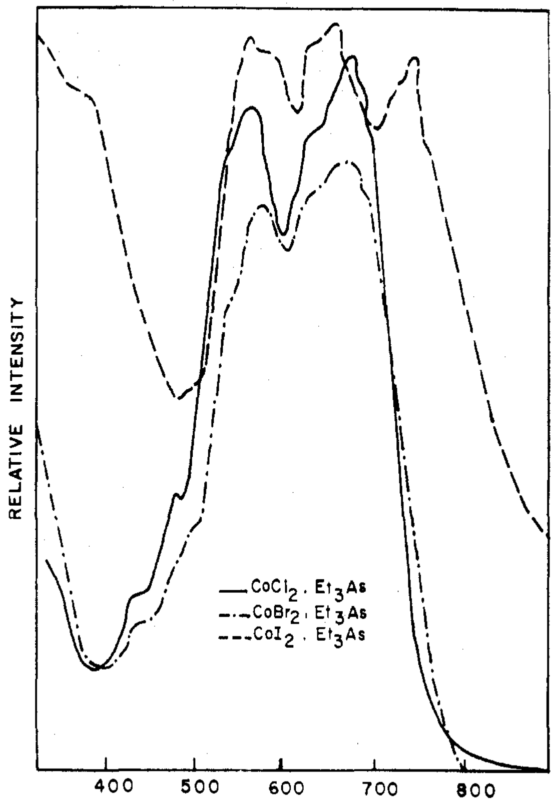
may be taken as a suggestive but not conclusive indication of relative donor ability. A more meaningful criterion of relative stability would be the value of P/P_0 for the reversible dissociation of a complex into the salt and the volatile base, but such values were too low to measure by the present experimental technique.

Several attempts were made to use competition reactions for an evaluation of the effects of metal and halide ions on the stability of the complexes. Samples of one metal halide and of a complex of another metal halide were placed in the arms of an inverted U tube. The tube was evacuated and sealed off and allowed to stand for several months. In no case was any transfer of base from one salt to another observed. No doubt this is a reflection of the exceedingly low dissociation pressures of the complexes, as is also indicated by



Wave length, mμ.

Fig. 4.—Reflectance spectrum of dichlorobis-(triethylarsine)-cobalt(II).



Wave length, mμ.

Fig. 5.—Reflectance spectra of μ-dihalodihalobis-(triethylarsine)-dicobalt(II) complexes.

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(17) G. E. Coates *J. Chem. Soc.*, 2003 (1951).

their negligible loss in weight when maintained at pressures lower than 1×10^{-4} mm. for several hours at room temperature.

Even with the less stable dihalobis-(triethylarsine)-cobalt(II) complexes, heating was required to cause rapid loss of base at these low pressures. At room temperature, these compounds lost half their arsine content when stored in a vacuum desiccator which was opened and re-evacuated several times over a 6-month period. The apparently greater stability of the dihalobis-(triethylarsine)-zinc(II) complexes is not a sufficient measure of relative Lewis acid strength, since the cobalt(II) compounds decompose into 1:1 complexes rather than simple salts. There is no evidence for the existence of 1:1 complexes in the zinc systems.

According to the criteria of Cotton and his coworkers,[18] all the cobalt(II) complexes reported here and previously[4] may be taken to be examples of tetrahedral coördination.

The magnetic moments correspond to spin-free cobalt(II) with appreciable orbital contributions. The extent to which the magnetic moments exceed the spin-only value of 3.87 B.M. is related to the value of Δ for the ligand field by the expressions[19] involving the Landé g factor

$$g = 2 + \frac{8\zeta}{3\Delta}$$

$$\mu_{\text{obs}} = g[S(S + 1)]^{1/2}$$

where ζ is the spin–orbit coupling constant. ζ is usually a few per cent lower[20] than the free ion value, which can be estimated from the width of the ground state multiplet.[18]

Nyholm[3] cites a personal communication from Jensen in which the value 3.5 B.M. is given for the magnetic moment of $CoCl_2 \cdot 2P(C_2H_5)_3$. The value found in this work, 4.4 B.M., is more reasonable theoretically and by analogy with similar compounds. The dipole moment of 8.7 D. reported by Jensen[2] for this compound is in accord with a tetrahedral structure.

The absorption at about 600 mμ of the cobalt(II) complexes is attributed[18] to the transition ν_3 from $^4A_2$ to $^4T_1$, these states arising from the ^4F ground state and ^4P first excited state of Co^{++} in a ligand field of tetrahedral symmetry T_d.

In the complexes CoL_2X_2 of symmetry C_{2v} or less, an "average" ligand field of tetrahedral symmetry may be taken in the first approximation, but as L varies in the sequence R_3N, R_3P, R_3As and as X varies in the sequence Cl, Br, I opportunities arise for major differences in Co–L and Co–X distances and the approximation of an average field becomes poor. This may be associated with increasing structure of the absorption band as can be seen in Fig. 3–5, and with spectral shifts due to the fact that Δ, or $(40/9)Dq$, is sensitive to interatomic distances. The visible absorption has been given[18] as $\nu_3 = (16/3)Dq + 14{,}540$ cm.$^{-1}$.

It is for this reason that the magnitudes of the orbital contributions to the magnetic moments and shifts in the value of λ_{cog} are not necessarily easily interpretable in terms of relative donor properties. It is not clear that the relative donor tendencies of the neutral compounds containing heavy donor atoms should be given by their positions in the spectrochemical series.[21]

A general understanding of the stoichiometries and stabilities of the complexes can be given in terms of a polarized ion–dipole model, with allowance made for the effect of obvious differences in molar volumes of ligand on the energy needed to expand the crystal lattice in the coördination reaction. The relative donor tendencies of the primary, secondary, and tertiary ethylamines toward calcium, cobalt(II), and zinc have been interpreted[4] in terms of such a model.

The energy of coördination may be taken as involving[22] ligand dipole–metal ion attraction, ligand charge–metal ion attraction, and various ligand–ligand repulsion terms, as well as induction energy and van der Waals repulsion terms, and other terms of the ordinary kind as in the Born equation. Considering the ligand dipole–metal ion attraction energy, it is important that while the dipole moment of an alkylamine is decreased with increasing degree of alkyl substitution, the reverse is true with the alkylphosphines.[23] Moreover, in the field of the poorly shielded nuclear charge of Co^{++}, the very much greater polarizabilities[23] of phosphines (and arsines) make it entirely reasonable that the

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(18) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961), and references therein.

(19) J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, Cambridge, 1961, p. 363.

(20) J. Owen, *Proc. Roy. Soc.* (London), **A227**, 183 (1955).

(21) J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 1047 (1959).

(22) R. E. Hamm, R. Kollrack, G. L. Welch, and R. H. Perkins, *J. Am. Chem. Soc.*, **83**, 340 (1961); R. E. Hamm, private communication.

(23) R. W. Parry and R. N. Keller, "Chemistry of the Coordination Compounds," J. C. Bailar, ed., Reinhold Publishing Co., New York, N. Y., 1956, chapter III.

sequence of total dipole moments should be $R_3N < R_3As \approx R_3P$. In terms of this model π-bonding would play a less significant role in understanding the relative donor abilities of these ligands toward transition metals.

This approach is continued in a description[24] of the relative donor tendencies of the primary, secondary, and tertiary ethylphosphines toward Co(II).

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[24] W. E. Hatfield and J. T. Yoke, *Inorg. Chem.*, **1**, 470 (1962).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 27, N. Y., AND THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS

Kinetics of the Reactions of Diethylenetriamineaquoplatinum(II) Ion with Different Ligands

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The rates of the reactions of $Pt(dien)H_2O^{2+}$ (dien = diethylenetriamine) with different ligands are reported and compared with the rates obtained for the reactions of the $Pt(dien)Br^+$ complex. A reagent independent rate, as well as a totally second order rate, is observed for the reaction of the aquo complex with Cl^- and NO_2^-. The mechanistic significance of this first-order rate is discussed. It is concluded that an aquo complex, formed by an SN2 reaction with water, is the principal intermediate in the totally first-order reactions of platinum(II) complexes.

Introduction

Ligand substitution reactions of square-planar metal complexes in solution have been found in general to exhibit a combination of first- and second-order rate behavior.[1-11]

The mechanism which leads to second-order kinetics can be visualized as a direct bimolecular reaction between the incoming ligand and the complex. However, although there is now considerable evidence that the first-order process involves the solvent to some degree, the extent of this solvent participation is unknown. In water solution the acid hydrolysis reaction completely accounts for the first-order rates found for $^{36}Cl^-$ exchange with different chloroplatinum(II) complexes, where sufficient kinetic data are available.[3-6] Thus an aquo complex must be involved as the first-order reaction intermediate in these cases.

Since the mechanism leading to the aquo complex intermediate is still a matter of speculation, it seemed desirable to study in detail the reaction rates of one particular aquo complex, $Pt(dien)H_2O^{2+}$, with a variety of different ligands. This complex was chosen since the reaction kinetics of the "parent" $Pt(dien)X^+$ (X = Cl, Br, I) complexes have been studied extensively.[8-10]

Experimental

A. **Materials.**—The $[Pt(dien)NO_3]NO_3$ complex used was prepared and analyzed as described earlier.[8] All other materials used were reagent grade.

B. **Determination of Reaction Rates.**—The Pt(dien)-H_2O^{2+} solutions were prepared by dissolving [Pt(dien)-

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