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# Preparation and Properties of a Series of Cobalt(II) Complexes

An undergraduate laboratory investigation

An introductory course in Ligand Field Theory is now an essential part of the undergraduate curriculum in inorganic chemistry. Such a course normally involves some discussion of so-called spectrochemical series where, on the basis of spectral data, ligands are arranged in order of their ability to induce d-orbital splitting. It is also usual to make mention of possible correlations between magnetic properties and structures of certain transition metal complexes. Since these topics were covered in a lecture course for third year undergraduate students at this university, it seemed highly desirable to allow students to investigate, in the laboratory, a series of related, easily prepared complexes which would provide an illustration of these and, if possible, similar topics. Various groups of transition metal complexes have been widely used to illustrate spectrochemical series. For example, the pentammine complexes of cobalt(III) are very useful for this purpose as is also the aqueous copper(II)-ammonia system (1). However, these systems cannot be used to demonstrate magnetic-structural correlations for which purpose another set of compounds must usually be employed (1).

The series of cobalt(II) complexes described in the present paper is ideally suited to provide, not only a demonstration of the influence of ligand field strength on the spectra of transition metal complexes and the use of magnetic measurements in structure determination, but also an excellent example of configuration equilibria in solution. The set of experiments described below have been a part of our laboratory course in inorganic chemistry for the past two years. The students had been introduced to the necessary theoretical concepts before carrying out the experiments which, moreover, also provided a useful vehicle for introducing undergraduates to the use and application of the spectrophotometer and Gouy balance. The series comprised four mixed complexes of cobalt-(II), namely  $Co(py)_2Cl_2$ ,  $Co(py)_2Br_2$ ,  $Co(py)_2I_2$ , and  $Co(2-mepy)_2Cl_2$  (where py is pyridine and 2-mepy is 2-methyl pyridine). The experiments are open-ended and can be extended, if desired, to include other closely related compounds such as  $Co(py)_2(NCS)_2$ , Co(3mepy)\_2Cl\_2, etc. The preparation of the complexes is described below. The products were analyzed for cobalt(II) by titration with standard 0.05 *M* EDTA solution using methyl thymol blue or xylenol orange as indicator (2). Analyses generally agreed to within  $\pm 2\%$  of the theoretical values.

## Preparation of Complexes

All preparations were carried out in the fume hood.

 $Co(py)_2Cl_2$ . 5 g of CoCl<sub>2</sub>·6H<sub>2</sub>O was dissolved in the minimum quantity of hot ethanol. To this solution was added dropwise with stirring a hot solution of 4 ml of pyridine in 5 ml of ethanol. The solution was cooled in an ice bath and the violet crystalline product collected using suction filtration. The product was washed with carbon tetrachloride and dried by gently heating under an infrared lamp or at 50–60°C in an oven.

 $Co(py)_2Br_2$ . 5 g of  $CoBr_2 \cdot 6H_2O$  was allowed to react with 5 ml pyridine in ethanol exactly as described for the chloro complex. The product was dried in air, finely powdered in a mortar, and heated in the oven at 50–60°C, or gently heated under an infrared lamp until completely bright blue in color.

 $Co(py)_2I_2$ . 7 g Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 8 g finely powdered KI were dissolved separately in minimum of hot ethanol. The two solutions were mixed and cooled in ice, and the KNO<sub>5</sub> was removed by filtration. The filtrate was evaporated to about one-tenth of the original volume under the infrared lamp, cooled, and filtered again. To the hot filtrate was added 7–10 g of hot pyridine. The mixture was cooled in ice and the precipitate which separated was filtered with suction, washed with hot carbon tetrachloride, and heated gently under an infrared lamp or in an oven at 50–60°C until all the solid was a blue-green color.

 $Co(2-mepy)_2Cl_2$ . This complex was obtained in an exactly analogous way to the pyridine analog. The bright blue product was washed with carbon tetrachloride and dried in air.

All the compounds were stored in a desiccator.

## **Magnetic-Structural Correlations**

The Gouy balance was calibrated using Hg[Co-(NCS)<sub>4</sub>] which had been prepared previously during the laboratory course. The magnetic moments of the complexes were determined in the usual way (3). Typical student values are listed in Table 1. The values correspond well with those published by Gill, Nyholm, and co-workers (4).

The magnetic moments of cobalt(II) complexes serve as a useful diagnostic tool for the differentiation of the four-coordinate tetrahedral and six-coordinate octahedral configurations. Moments for tetrahedral complexes lie in the range 4.2–4.8 BM while those for octahedral complexes usually lie in the range 4.8–5.4 BM (5). Students were asked to comment on the values observed for the series. In the Co(py)<sub>2</sub>Cl

Table 1. Magnetic Moments in Bohr Magnetons

Complex	Typical student values measured in the range 23–27°C	Published values measured in the range 16–20°C
$Co(py)_2Cl_2$	5.15	5.15 (4)
$\mathrm{Co}(\mathrm{py})_2\mathrm{Br}_2$	4.49	4.50(4)
$Co(py)_2I_2$	4.45	4.47(4)
$Co(2\text{-mepy})_2Cl_2$	4.47	4.48(8)

Table 2.	Wavelengths of Maximum
Absorption	$(\lambda_{max})$ in Chloroform Solution

Complex	$\lambda_{max}$ (m $\mu$ )		
$Co(py)_2Cl_2$	605		
$Co(py)_2Br_2$	650		
$Co(py)_2I_2$	690		
$Co(2\text{-mepy})_2Cl_2$	640		

Table	3.	Equi	ibri	um	Constant	s (	and	Free	
Energy	Cha	inges	for	Co	onfiguratio	on	Equ	Jilibri	a

Complex	Typical stu values at 2	ident 25°C	Published values at 20°C (8)		
	K	$\Delta G^{\circ}$ kcal/mol	K	$\Delta G^{\circ}$ kcal/mole	
Co(py) <sub>2</sub> Cl <sub>2</sub>	12.0	-1.46	12.6	-1.48	
Co(py)2Br2	8.8	-1.28	9.04	-1.28	
$Co(py)_2I_2$	1.7	-0.31	2.32	-0.49	
Co(2-mepy) <sub>2</sub> Cl <sub>2</sub>	Immeasurably small		Immeasurably small	• • •	



Absorption spectra of  $10^{-3}M$  solutions in chloroform of A, Co(py)<sub>2</sub>Cl<sub>2</sub>, B, Co(py)<sub>2</sub>Br<sub>2</sub> and C, Co(py)<sub>2</sub>l<sub>2</sub>.

complex, a six-coordinate polymeric octahedral structure is attained by bridging through the chlorine atoms which accounts for the higher magnetic moment observed for this complex (4).

#### Spectra

The concept of *d*-orbital splitting in a ligand field had been covered in lectures, and students were familiar with the energy level diagrams for octahedral and tetrahedral cobalt(II) complexes (6). The complexes described dissolve in chloroform to give blue or bluegreen solutions in which they exist as discrete tetrahedral molecules. The absorption in the 580–700 m $\mu$ region, which accounts for the blue or green colors, is due to the  ${}^{4}A_{2} \rightarrow {}^{4}T_{1}$  (P) transition (7). The intensities of these bands are much higher than for octahedrally coordinated cobalt(II), and molar absorptivity constants of the order 500-1200 are usual. Students were asked to measure the spectrum of a  $10^{-3}$  M solution in chloroform of each complex over the range 500-800  $m\mu$ , to note the wavelength of maximum absorption,  $\lambda_{\text{max}}$ , and, from these values, to place the ligands' Cl, Br, I in a series according to their capacity to induce d-orbital splitting. The spectra are shown in the figure and  $\lambda_{\max}$  values are listed in Table 2.

## Measurement of Equilibrium Constants

If pyridine is added to a chloroform solution of one of the  $Co(py)_2X_2$  complexes (where X = halogen), a configuration equilibrium is set up between the tetrahedral  $Co(py)_2X_2$  species and its octahedral adduct,  $Co(py)_4$ - $X_2$ 

$$Co(py)_2 X_{2(tet)} + 2py \rightleftharpoons Co(py)_4 X_{2(oct)}$$
 (1)

The octahedral species exhibits much less intense absorption (molar absorptivity constants 5–10) at shorter wavelengths (480–550 m $\mu$ ) than the tetrahedral complexes. It is therefore possible to determine the equilibrium constant, K, for reaction (1) by a spectrophotometric method as outlined below.

A set of solutions of known concentrations in  $\text{CoL}_2X_2$ were prepared (usually between  $10^{-3}-10^{-4}$  M). A plot of concentration against absorbance at  $\lambda_{max}$  was measured. (All the complexes obey Beer's law.) A corresponding set of solutions containing exactly the same concentrations of  $\text{CoL}_2X_2$  as before but containing also a known excess of amine, L (0.4–0.8 M), was prepared. The decrease in absorbance at  $\lambda_{max}$  for  $\text{CoL}_2X_2$ due to the addition of amine is a measure of the amount of  $\text{CoL}_2X_2$  transformed into the  $\text{CoL}_4X_2$  adduct and thus permits the calculation of K as follows

Let A be the total concentration of  $\operatorname{CoL}_2X_2$  before reaction. Let B be the total concentration of amine, L, before reaction. Let x be the concentration of  $\operatorname{CoL}_4X_2$  formed at equilibrium. At equilibrium we have

$$\operatorname{CoL}_2 X_2 + 2L \rightleftharpoons \operatorname{CoL}_4 X_2$$
  
 $[A - x] \quad [B - 2x] \quad [x]$ 

and

$$K = \frac{[x]}{[A - x][B - 2x]^2}$$

A is known; [A - x] is found by measuring the absorbance at  $\lambda_{max}$  and by interpolation from the calibration graph, hence [x] can be obtained. Similarly, since B is known, the concentration

of "free" ligand [B - 2x] can be found. Since K is relatively small for these complexes [B - 2x] can be simply taken to be equal to [B].

As a useful exercise students were asked to calculate from K the corresponding free energy changes,  $\Delta G^{\circ}$ , for the reactions (from  $\Delta G^{\circ} = -RT \ln K$ ). Average Kand  $\Delta G^{\circ}$  values obtained are presented in Table 3. These values compare well with those in the literature (8).

Students were then asked to put forward a reasonable explanation for the decrease in the value of K on going from  $X = Cl^-$  to  $Br^-$  to  $I^-$  and the non-formation of a  $Co(2-mepy)_4Cl_2$  complex. A number of reasons can be put forward to explain the former. First of all, the decrease in K values is in line with increasing polarizability of X. Since  $I^-$  is more polarizable than  $Cl^-$ , it is to be expected that the metal ion in the complex  $Co(py)_2I_2$  will be closer to electroneutrality than in  $C_0(py)_2Cl_2$  and will therefore have a smaller tendency to take up two additional molecules. Secondly, it may also be argued that from steric considerations, K is also in the expected order for the halides. Since the iodide ion is larger than the chloride ion, it follows that the incoming pyridine molecules find it easier to become attached to the  $Co(py)_2Cl_2$  than to the  $Co(py)_2I_2$  mole-

This proved to be the most popular student cule. explanation and, on the basis of the few results obtained this was quite reasonable. However, thermodynamic investigations on these and a variety of related systems indicate that it is probably a small  $\pi$ -contribution to the metal-amine bond in the octahedral adduct which plays a dominant role rather than steric or polarizability factors (8). The non-formation of Co(2-mepy)<sub>4</sub>Cl<sub>2</sub> suggests that substitution in the 2-position introduces a steric barrier to addition of two further 2-methyl pyridine molecules to a  $Co(2\text{-mepy})_2Cl_2$  complex (9).

## **Literature Cited**

- ADAMS, D. M., AND RAYNOR, J. B., "Advanced Practical Inorganic Chemistry," John Wiley and Sons Ltd., London, 1965, p. 142 and 151.
   VOGEL, A. I., "A Textbook of Quantitative Inorganic Analysis," third
- ed., Longmans-Green & Co. Ltd., London, p. 443. agus, B. N., AND LEWIS, J., "Modern Coordination Chemistry,"
- (3) FIGGIS, B. N., AND LEWIS, J., "Modern Coordination Chemistry," (*Editors:* LEWIS, J., AND WILKINS, R. G.), Wiley-Interscience, New York, 1960, ch 6. (4) GILL, N. S., NYHOLM; R. S., BARCLAY, G. A.,
- CHRISTIE, T. I. AND (4) GILL, N. S., NYHOLM; R. S., DARCLAT, G. A., CHAISTE, T. T. A.P. PAULING, P. J., J. Inorg. Nucl. Chem., 18, 88 (1961).
  (5) FIGGIS, B. N., AND NYHOLM, R. S., J. Chem. Soc., 12 (1954); FIGGIS, B. N., AND NYHOLM, R. S., J. Chem. Soc., 331 (1959).
  (6) ORGEL, L. E., "An Introduction to Transition-Metal Chemistry," (20-14) Mathematics Co. 144 London 1066, p. 91.

- (6) ORGEL, L. E., "An Introduction to Transition-Metal Chemistry," (2nd ed.), Methuen & Co. Ltd., London, 1966, p. 91.
  (7) COTTON, F. A., AND WILKINSON, G., "Advanced Inorganic Chemistry," (2nd ed.), Wiley-Interscience, New York, 1966, p. 872.
  (8) KING, H. C. A., KOROS, E. AND NELSON, S. M., J. Chem. Soc., 5449 (1963).
  (9) ALLAN, J. E., BROWN, D. H., NUTTALL, R. H. AND SHARP, D. W. A., J. Inorg. Nucl. Chem., 26, 1895 (1964); KING, H. C. A., KOROS, E. AND NELSON, S. M., J. Chem. Soc., 4832 (1964).