

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Reflection Spectra of Some Solid Cobalt(II) Salts in the Visible Region

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Reflection spectra are presented for a number of solid hydrates and pyridinates of cobaltous salts, and for double salts of cobaltous chloride with cesium chloride and pyridinium chloride. Correlations between the solid and solution spectra, and crystal structures, are pointed out.

There seems little reason to doubt any more that the "red" or "pink" solutions of cobaltous salts are associated with the six coördinate condition, and the "blue" solutions with the four coördinate condition.¹ The correlations of the colors of the cobalt halide solids are less obvious, in particular since intermediate colors are found, and in some instances two distinct color phases are known for the same analytical composition. Furthermore, the stoichiometry of the solid material does not correspond to the cobalt coördination number in the crystalline solid in cases other than the simple hexahydrate or analogous compounds. This consideration would not be important if crystal structures were known for all the relevant compounds. We have investigated the reflection spectra of a number of powdered solid cobalt(II) compounds, and have found correlation with the solution spectra and with such crystal structure data as are available, which furnishes basis for conclusions about the structures not yet determined crystallographically.

Experimental

Hydrates and pyridinates of cobaltous nitrate and chloride, and dipyrindinium cobaltous tetrachloride, were prepared as previously described.² The first crop of crystals from an aqueous solution made with 11 g. of CsCl and 5 g. of cobaltous chloride hexahydrate gave Cs_2CoCl_4 with some 20% of Cs_3CoCl_5 , while a second crop gave large crystals of the tricesium form,^{3,4} determined by cobalt analyses. Both of these solids were studied.

Powdered solid was distributed thinly and evenly as practical on the gummed surface of transparent adhesive tape which was then fastened to white cardboard and mounted in the reflection spectrum attachment of the Beckman Model DU spectrophotometer for measurement. A similar strip of tape without cobalt salts added was used as the blank. Results of a number of such measurements are given in Figs. 1-3. It should be pointed out that in the case of spectra with considerable intensity differences between peaks and shallows (*e.g.*, those in Fig. 2) variations in sample optical thickness over the area covered by the light beam result in exaggeration of the heights of the minor peaks relative to the major, whose effective optical density is limited by the amount of "whiteness" seen by the light beam. Preparations of different "thickness" will therefore give different prominence to the minor peaks, and ratios of intensities between peaks cannot be relied on. It is sufficient for the purposes of this paper, however, to be able to compare the locations, shapes and approximate relative intensities of the peaks found.

We are indebted to Mr. John R. Ferraro for necessary cobalt analyses.

Discussion

For cobaltous nitrate or perchlorate hexahydrate (curves VI and VII, Fig. 1) the spectra are indis-

tinguishable and are very similar to that of the salt in water,⁵ though the peak is shifted to about 505 $m\mu$ from the value 510 $m\mu$ in solution. The spectrum of the nitrate dihydrate (curve IV) is rather similar, but the intensity of the 505 $m\mu$ component of the peak has apparently suffered with respect to one at shorter wave lengths, so there appear to be peaklets at 500 and 480 $m\mu$, the dip being extremely shallow. Cobaltous chloride hexahydrate shows more opacity and more scarlet in its coloration, and the spectrum (curve V) shows this to be due to an additional strong absorption at 540 $m\mu$. The shorter wave length component seen in curves VI and VII has apparently shifted to still shorter wave lengths, giving distinct peaks at 505 and 460 $m\mu$. A very similar spectrum, but with an over-all shift to shorter wave lengths, is shown by $\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O} \cdot 2\text{Py}$ (curve I). The cobaltous nitrate pyridinates seem to differ little if at all from each other (the dipyrindinate was probably a thick preparation) and are distinguished from the hexahydrate primarily by shifts to longer wave lengths and an increased suggestion of structure.

These are unquestionably "red" salts. Typical blue forms may be expected to be salts like Cs_3CoCl_5 , for which the existence of CoCl_4^- complex groups has been demonstrated crystallographically,⁴ and Cs_2CoCl_4 and $(\text{HPy})_2\text{CoCl}_4$ for which^{2,6,7} the group may be assumed, and all of which are deep blue in color. Measurements on the three compounds show that they are characterized by an intense peak centering at about 660 $m\mu$, with a series of less intense sharp peaks at shorter wave lengths (about 532, 452 and 410 $m\mu$), spectra which are very like that of the CoCl_4^- complex in solution.⁸⁻¹⁰ There are differences between the spectrum of $(\text{HPy})_2\text{CoCl}_4$ and the cesium double salts, notably in the structure of the major peak, which may be ascribable to crystal structure effects. The particular curve for the pyridinium salt plotted (III, Fig. 2) is intermediate between one from a "thinner" sample, which shows the 535 $m\mu$ peak at a lower intensity relative to the main peak, and a "thicker" preparation showing another peak at about 455 $m\mu$, in correspondence to the spectra of the cesium salts. Plot of part of a "thick" preparation of a cesium double-salt (I of Fig. 2) is given to show detail in the low-intensity region of the spectrum, while a "thinner" preparation (curve II) depicts better the relation of the major

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- (3) G. F. Campbell, *Am. J. Sci.*, **48**, 419 (1894).
- (4) H. M. Powell and A. F. Wells, *J. Chem. Soc.*, 359 (1935).

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- (10) A. V. Kiss and M. Gerendas, *Z. physik. Chem.*, **180**, 117 (1937).

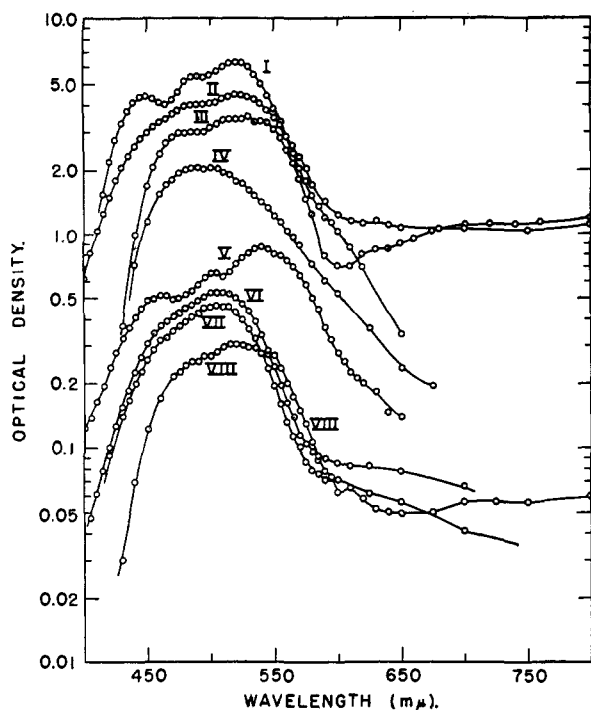


Fig. 1.—Reflection spectra of solid Co(II) "red" compounds. Ordinates arbitrary, scale indicating differences for optical density ratio of 10. I, $\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O} \cdot 2\text{Py}$; II, $\text{Co}(\text{NO}_3)_2 \cdot 2\text{Py}$; III, $\text{Co}(\text{NO}_3)_2 \cdot 3\text{Py}$; IV, $\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$; V, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$; VI, $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$; VII, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; VIII, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{Py}$.

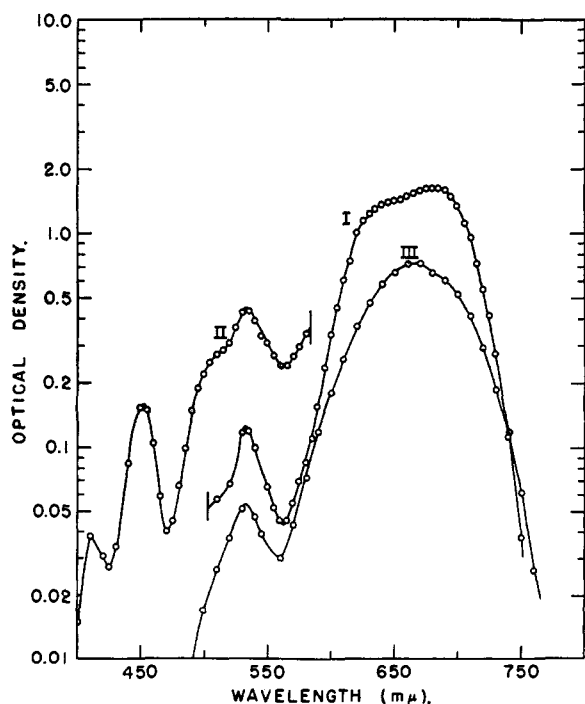


Fig. 2.—Reflection spectra of solid blue Co(II) double chlorides. Ordinates arbitrary, scale indicating differences for optical density ratio of 10. I, II, preparations of Cs_2CoCl_4 ; III, $(\text{HPy})_2\text{CoCl}_4$.

peak to the minor ones, and the structure of the major peak. The wave lengths of the minor peaks

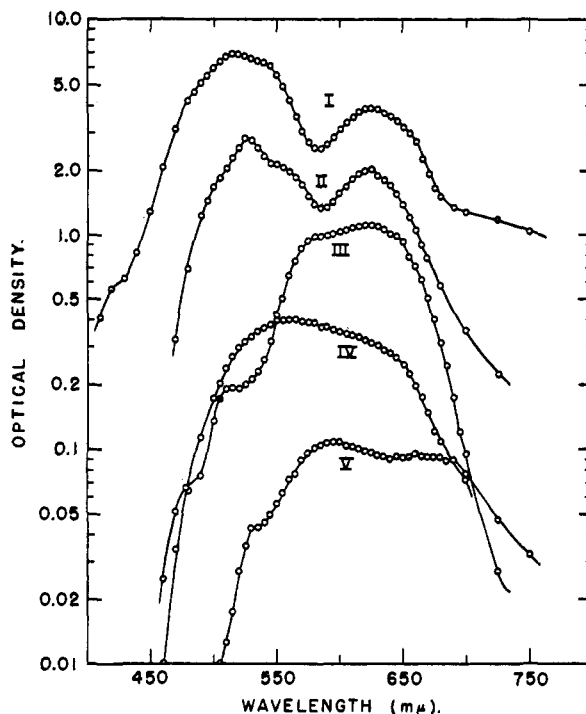


Fig. 3.—Reflection spectra of some violet and blue CoCl_2 compounds. Ordinates arbitrary, scale indicating differences for optical density ratio of 10. I, $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ (violet); II, $\text{CoCl}_2 \cdot 2\text{Py}$ (violet); III, $\text{CoCl}_2 \cdot 2\text{Py}$ (blue); IV, $\text{CoCl}_2 \cdot \text{H}_2\text{O}$; V, CoCl_2 (with CaSO_4).

compare quite closely with the peaks for HCl solution found, for example, by Kiss and Gerendas.¹⁰ Earlier literature^{11,12} on the spectrum of $(\text{HPy})_2\text{CoCl}_4$ allows comparison only to the extent that it indicates possible existence of some peak at or below about 530 $\text{m}\mu$.

The hydrates and pyridinates of cobaltous chloride with two or fewer of these groups per cobalt form an interesting series (Fig. 3). The "violet" form of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ shows a principal peak centering at about 520 $\text{m}\mu$, with a secondary peak at about 625 $\text{m}\mu$ masking the otherwise magenta or "red" color to a violet. The dipyridine "violet" form shows a very similar spectrum, the major peak (with a suggestion of structure, as in the other pyridinates) coming at 525 $\text{m}\mu$, and the secondary peak at 625 $\text{m}\mu$. The "blue" form of the dipyridinate shows a markedly different spectrum (curve III), with the major absorption at 625 and 580 $\text{m}\mu$, and minor peaks suggested at about 510 and 480 $\text{m}\mu$. Comparison will show that this spectrum is very close to that of the compound in acetone solution,¹ which has been shown to be due to a 4-coordinate entity. Electron diffraction determination of the crystal structure¹³ of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ has shown the cobalt to be 6-coordinate, in agreement with the interpretation of the spectrum. The published studies of the structure of violet $\text{CoCl}_2 \cdot 2\text{Py}$ do not give a complete structure,¹⁴ but allow an interpre-

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(13) B. K. Vainshtein, *Doklady Akad. Nauk S. S. S. R.*, **68**, 301 (1949).

(14) E. G. Cox, A. J. Shorter, W. Wardlaw and W. J. R. Way, *J. Chem. Soc.*, 1556 (1937).

tation¹⁵ of octahedral coordination. The structure of the blue form of the compound has not been deciphered but it is isomorphous with the corresponding bromide and iodide¹⁴ for which only blue forms are known. The hypothesis that these are tetrahedral rather than octahedral cobalt structures, based on the correspondence of the spectra of the solid and the entity in solution, seems reasonable.

Cobaltous chloride monohydrate is a blue-violet solid, whose absorption parallels roughly that of the "violet" forms above, but combines the two peaks of the latter in a single broad absorption. The flat maximum in the absorption comes at about 560 m μ . Anhydrous cobaltous chloride (in the presence of calcium sulfate, to maintain its anhydrous state) has a principal peak at about 600 m μ , with a suggestion of structure in the region from 640–690 m μ . A minor peak is indicated about 535 m μ . The color is a very pale blue, compared to the rich blue of the salts with the CoCl₄⁼ grouping. Crystallographic investigation has assigned the solid the CdCl₂ structure,¹⁶ with the cobalt being 6-coordinate. It seems reasonable to conclude, therefore, that the spectra of the anhydrous chloride and of the monohydrate represent further extension of the difference between the violet dihydrate or dipyridinate and the hexahydrated or hexapyridinated forms, and that the spectral shift leading to visual blueness may be ascribed to the mass effect of coordination predominately to chloride rather than oxygen or nitrogen. An analogous shift of spectrum to longer wave lengths is seen on comparing the spectra of solutions of cobalt chloride,

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bromide and iodide in the respective hydrogen halide acids.⁹

In the case of glasses, pigments, etc., in which cobalt is a minor component, it has already been proposed that the blue or red color of the substance is correlated with the 4-coordination or the 6-coordination of the basic lattice structure.^{17–20} In summary, therefore, one may say that the Co(II) solids which are red or pink certainly have 6-coordinate cobalt; the violet forms of the composition CoX₂·2S (X = halide, S = molecular base) are most probably all 6-coordinate also; and most of the blue forms are 4-coordinate. The exceptions to the last are blue solids in which 6-coordinate cobalt is attached predominately to heavy atoms, such as Cl and heavier. In the case of the violet CoX₂·2S forms it does not seem too likely that the secondary long wave length peak signalizes the presence of two kinds of cobalt atoms in the solids, with some small proportion (perhaps just at the crystal surface) coordinated to only 4 groups. The more probable explanation is that the secondary peak represents a displacement of one of the peaks not so well resolved in the hexapyridinate spectrum.

Added Note.—Since the above report was written, it has been possible to prepare a sample of Cs₂CoCl₄ in a non-absorbing matrix for transmission measurements at considerably higher resolution than was possible for the reflection spectra. This material, observed both at room temperature and at liquid nitrogen temperature, shows a wealth of structural details otherwise unobserved, and will be the subject of a separate report.

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Mass Spectra of Six Lactones¹

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Mass spectra are given for the aliphatic lactones, β -propio, γ -butyro, γ -valero, γ -crotono, β -angelica and α -angelica. For four of the lactones spectra were also obtained of samples with carbonyl oxygens containing enriched O¹⁸. A detailed discussion of the data is given and it is concluded that the main peaks of the spectra result from splitting of two alternate bonds of the lactone rings. The stability of the parent molecule ions is greater with the unsaturated lactones and their spectra are characterized by larger intensity of peaks due to rearrangement. Although there are frequent large variations in yields of particular ions, the spectra for both the saturated and the unsaturated lactones arise from similar bond splitting processes.

This paper gives the mass spectra of six simple aliphatic lactones, three saturated and three unsaturated. Five of the lactones are five-membered rings and one, β -propiolactone, is a four-membered ring. Figure 1 gives the structures of the six lactones. The ring bonds are numbered for convenience in later discussions.

The mass spectral data have been examined in some detail from the standpoint of the most probable ion dissociation processes. This approach has led to fairly definite conclusions about the origins of

the majority of the peaks and to a good qualitative correlation of spectra with molecular structure. A further object of this study was to provide knowledge for interpretation of the mass spectrum of diketene; this problem will be considered in a subsequent communication.

Experimental

Materials and Procedure.—The mass spectrometer analyses were made using a General Electric mass spectrometer. Spectra were scanned magnetically using 2000 v. ion accelerating potential and an electron accelerating potential of 50 v. Mass assignments were made independently using H₂O⁺, CO₂⁺ and the Hg⁺⁺ background in the machine as

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