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Studies on the Stepwise Controlled Decomposition of 2,2'-Bipyridine Complexes of Cobalt(II) and Nickel(II) Chlorides

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Stepwise controlled thermal decomposition of the compounds $[\text{Ni}(\text{bipy})_3]\text{Cl}_2 \cdot 7\text{H}_2\text{O}$ and $[\text{Co}(\text{bipy})_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (bipy = 2,2'-bipyridine) has yielded compounds of the following formulas, where M = both Ni and Co: $\text{M}(\text{bipy})_2\text{Cl}_2$, $\text{M}_3(\text{bipy})_4\text{Cl}_6$, $\text{Ni}(\text{bipy})\text{Cl}_2$, α - and β - $\text{Co}(\text{bipy})\text{Cl}_2$ (two distinct stereochemical configurations), $\text{Co}(\text{bipy})_{0.80}\text{Cl}_2$, and $\text{M}(\text{bipy})_{0.50}\text{Cl}_2$. Structures have been assigned to most of these compounds on the basis of analytical data, electronic absorption spectra, magnetic moments, conductance data, and X-ray powder diffraction patterns, as well as by analogy to pyridine analogs of known structures. All cobalt-nickel analogous pairs, except $\text{M}(\text{bipy})_2\text{Cl}_2$, have been shown to be isomorphous.

Relatively little is known about bipyridine-bipositive transition metal complexes containing fewer than three ligands per metal ion. Pfeiffer and Tappermann¹ first reported the compound $\text{Ni}(\text{bipy})_2\text{Cl}_2$, and a series of bis(2,2'-bipyridine) nickel(II) complexes has since been described by Harris and McKenzie.² All of these complexes were found to have octahedral coordination. No cobalt compounds of this type appear to have been reported.

Only a few compounds of the general formula $\text{M}(\text{bipy})\text{X}_2$ are known. Yamasaki³ has reported a green compound of the composition $\text{Co}(\text{bipy})\text{Cl}_2$, and also a blue-violet complex of the same composition. Ocone, Soulen, and Block⁴ have carried out a study of the thermogravimetric behavior of the blue $\text{Co}(\text{bipy})\text{Cl}_2$ and have found that a substance of the approximate composition $\text{Co}(\text{bipy})_{0.8}\text{Cl}_2$ could be obtained. Broomhead and Dwyer⁵ have described the preparation of dichloromonobipyridine complexes of bipositive manganese, nickel, and iron. No structural information is available on the $\text{M}(\text{bipy})\text{Cl}_2$ complexes.

In a study of the thermal decomposition of tris(2,2'-bipyridine) complexes of some bipositive 3d transition elements, Dhar and Basolo⁶ reported the isolation of the compound $\text{Ni}(\text{bipy})_{1.80}\text{Br}_2$, which was formulated as $[\text{Ni}(\text{bipy})_3]\text{NiBr}_4$.

The current communication is concerned with the isolation and characterization of the products obtained by the stepwise controlled thermal decomposition of $[\text{Ni}(\text{bipy})_3]\text{Cl}_2 \cdot 7\text{H}_2\text{O}$ and $[\text{Co}(\text{bipy})_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$. A number of new species containing fewer than three bipyridine ligands per metal atom are described, and striking parallelisms in the two systems are demonstrated.

Experimental

Materials.—The following substances were used as obtained from the manufacturer without further purification: 2,2'-bi-

pyridine, Matheson Coleman and Bell, m.p. 69–70°; nickel(II) chloride 6-hydrate, C.P. Baker Analyzed Reagent, cobalt content 0.001%; cobalt(II) chloride 6-hydrate, Baker Analyzed Reagent, nickel content 0.002%; tetraphenylarsonium chloride, Eastern Chemical Corp.; absolute ethanol, commercial bulk solvent; N,N-dimethylformamide, Matheson Coleman and Bell, Spectro-quality Reagent; acetonitrile, Fisher Certified Reagent, water content 0.3%; acetone, Baker Analyzed Reagent, water content 0.38%; Linde dry nitrogen.

Matheson Coleman and Bell nitrobenzene was passed through a column (1 in. diameter) of Woelm neutral activated alumina. The purified solvent, specific conductance 4.7×10^{-8} ohm⁻¹ cm.⁻¹, was stored in a dark, air-tight bottle. Nitromethane, Fisher Certified Reagent, water content 0.00%, had a specific conductance of 2.25×10^{-8} ohm⁻¹ cm.⁻¹ after fractional crystallization.

Samples of anhydrous nickel(II) chloride were supplied by Mr. William H. McMahan of our laboratory. Anhydrous cobalt(II) chloride was obtained simply by heating the 6-hydrate at 150° for several hours. Only a negligible amount of cobalt(II) hydroxide appeared in the product as a result of hydrolysis. Tetraphenylarsonium tetrachloronickelate(II) and tetraphenylarsonium tetrachlorocobaltate(II) were prepared by evaporating solutions, each of about 1 g. of the metal chloride 6-hydrate and the stoichiometric amount of tetraphenylarsonium chloride in 50 ml. of absolute ethanol, to about 5 ml. The mixtures were chilled and the products were filtered, washed with 5 ml. of cold absolute ethanol, and dried in air at 110°.

$[\text{Ni}(\text{bipy})_3]\text{Cl}_2 \cdot 7\text{H}_2\text{O}$ and $[\text{Co}(\text{bipy})_3]\text{Cl}_2 \cdot 7\text{H}_2\text{O}$ were prepared in 85–90% yields from the bipositive metal halide 6-hydrate according to the method of Morgan and Burstall.⁷ Removal of water from $[\text{Co}(\text{bipy})_3]\text{Cl}_2 \cdot 7\text{H}_2\text{O}$ under vacuum ($\sim 10 \mu$) at room temperature yielded $[\text{Co}(\text{bipy})_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$.

Analytical Methods.—It was observed that the chloride in all the compounds prepared was released as free chloride ion in acidic aqueous solution. Chloride, therefore, was determined by potentiometric titration with 0.1 M silver nitrate in strongly acidic solution, using a glass reference electrode and a Ag–AgCl indicator electrode.

Nickel was determined by precipitation as the dimethylglyoximate complex from strongly ammoniacal solution. The presence of 2,2'-bipyridine did not interfere in the analysis.

Cobalt was determined gravimetrically as CoSO_4 . The sample was first fumed to dryness with concentrated sulfuric acid on a hot plate and then ignited at red heat over a gas flame for 1 hr. The mixture of sulfate and oxides which formed was fumed to dryness with concentrated sulfuric acid on a hot plate, and the residue was heated in a muffle furnace for 12 hr. at 510° and then cooled and weighed.

In the conversion of one compound to another by controlled thermal decomposition, bipyridine was evolved. Weight loss

(1) P. Pfeiffer and F. Tappermann, *Z. anorg. allgem. Chem.*, **215**, 273 (1933).

(2) C. M. Harris and E. D. McKenzie, *J. Inorg. Nucl. Chem.*, **19**, 372 (1961).

(3) K. Yamasaki, *Bull. Chem. Soc. Japan*, **15**, 130 (1940).

(4) L. R. Ocone, J. R. Soulen, and B. P. Block, *J. Inorg. Nucl. Chem.*, **15**, 76 (1960).

(5) J. A. Broomhead and F. P. Dwyer, *Australian J. Chem.*, **14**, 250 (1960).

(6) S. K. Dhar and F. Basolo, *J. Inorg. Nucl. Chem.*, **25**, 37 (1963).

(7) G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 2213 (1931).

data were therefore significant in the total analytical picture.

Visible and Near-Infrared Absorption Spectra.—All spectral measurements were made with a Cary Model 14 recording spectrophotometer. All measurements made on solutions were purely routine, but the technique used in obtaining absorption spectra of solid compounds in the form of Nujol mulls apparently is a new one and is, therefore, described in some detail.

The method was suggested by a report by Cotton, Goodgame, Goodgame, and Sacco⁸ that spectra could be taken in Nujol mulls mounted in the spectrophotometer in the conventional way, but using filter paper soaked in the oil as a scattering agent in both the sample and reference beams of the spectrophotometer. No details were given regarding the design of the sample cell itself.

In our method, about 25–50 mg. of the solid sample was finely ground with a small agate mortar and pestle. One drop of Nujol was added to the sample, and grinding was continued until the sample was thoroughly wet. Another three or four drops of Nujol were added, and the suspension was mixed by grinding until it appeared homogeneous. The mull was then painted onto a piece of Whatman No. 1 filter paper over an area sufficiently large to cover the light beam completely. The strip of paper bearing the sample was then sandwiched between two pieces of 0.95-cm. plywood or fiberboard into which were cut windows large enough to permit passage of the light beam. The dimensions of the outer edges of the sample holder were cut to fit the design of the sample compartment of the instrument. The holder of the Nujol-soaked reference strip was of the same design.

The sample and reference "cells" were then placed in positions as close as possible to the detector, so that a minimum of scattered light leaving the sample would be lost. From this point onward, the spectrum was obtained as one would the spectrum of a sample in solution. The intensities of the absorption bands could be raised or lowered relative to the base line by increasing or decreasing the thickness of the mull on the filter paper. Very intense absorptions in the ultraviolet region could be observed by using a very thin coating of sample on the filter paper strip.

The method was found to be applicable over the wave length region from 200 to 1700 $m\mu$. Beyond 1700 $m\mu$, strong interference was observed, which was probably due either to the Nujol or filter paper. Very small interferences, which covered a width of 5–10 $m\mu$ each, were observed at 980, 1260, and 1380 $m\mu$. However, since the absorption bands observed for most transition metal complexes are quite broad (300–500 $m\mu$) in these regions, these irregularities presented no problem in the interpretation of the spectra. The degree of resolution obtained appeared to be rather insensitive to the extent of grinding of the solid, the homogeneity of the mull, and the extent to which the mull covered the light beam.

In measuring the spectrum of anhydrous cobalt(II) chloride, special precautions had to be taken to exclude moisture, toward which the compound is extremely sensitive. The sample was mixed with an approximately equal portion of phosphorus(V) oxide and the mull with Nujol prepared in a drybox. The spectrum was then run as rapidly as possible (about 5 min.). Change in color of the chloride due to attack by atmospheric moisture was negligible over this short period of time.

Magnetic Susceptibility Measurements.—These measurements were made by the Gouy method. The susceptibility of each compound prepared was determined by comparison with the known susceptibility of $Hg[Co(SCN)_4]$. Appropriate diamagnetic corrections were made in each case.

Electrolytic Conductance Measurements.—Conductance measurements were carried out using an Industrial Instruments Model RC-16B2 bridge with conventional dip-type cells. The electrodes were platinized. Measurements on solutions of compounds in nitrobenzene were made with a cell which had a cell constant of 0.927 cm^{-1} . All other measurements were made with a cell which had a cell constant of 0.0990 cm^{-1} . Molar conductance values are expressed in the conventional units, $ohm^{-1} mole^{-1} cm^2$.

X-Ray Powder Diffraction Patterns.—X-Ray patterns of the

powdered samples were obtained with a North American-Phillips X-Ray unit with its standard diffractometer accessory. When patterns of $Ni(bipy)Cl_2$ and $Co(bipy)_{0.80}Cl_2$ were taken, the entire shielding apparatus (in which the sample was located at the center) was enclosed with polyethylene film, and a stream of dry nitrogen was passed continuously over the sample during the course of measurement.

Both Cr $K\alpha$ and Cu $K\alpha$ radiation were used. With the chromium target, a voltage of 35 kv., a current of 9 ma., and a vanadium filter were employed. With the copper target, a voltage of 45 kv., a current of 15 ma., and a nickel filter were used. Scanning speed was $1^\circ min^{-1}$ (2θ).

General Technique for the Thermal Decomposition Experiments.—Heating was effected in a tubular Haskins electric furnace, 31 cm. long and 3.3 cm. in diameter. The furnace was hinged to permit convenient manipulation and observation. The temperature was measured by means of a chromel–alumel thermocouple whose hot junction was located against the outer wall of the Pyrex tube which contained the sample boat. The temperature was controlled within a 3° range by means of a Wheelco Model 407 temperature controller with a Model 610 pilot amplifier.

The sample (3–5 g. in each case) was contained in a Coors No. 8 glazed porcelain boat which was placed in a Pyrex tube of 30-mm. diameter in such a manner that both the hot junction of the thermocouple and the center of the sample were equidistant from either end of the furnace.

In cases where nitrogen was passed over the sample during the heating process, the Pyrex tube was 48 cm. long and was fitted at each end with one-hole rubber stoppers, through which the nitrogen passed. The end of the tube toward the nitrogen exit protruded 16 cm. past the end of the furnace and served as a condenser for the bipyridine vapor evolved during the reaction. The nitrogen leaving the reaction tube was passed through a concentrated sulfuric acid tower which served as a flow-rate gauge. The flow rate (from a 7-mm. i.d. tube) was 1–2 bubbles per second.

When reactions were carried out *in vacuo*, the Pyrex reaction tube was closed at one end and was of sufficient length (36 cm.) so that about 16 cm. protruded from the furnace to provide a condenser for the bipyridine liberated. Attached to the protruding end of the tube was a 3/4/45 ground glass inner joint. This tube was provided with a cap made from a 3/4/45 outer joint to which was attached a stopcock leading to a Dry Ice–acetone cold trap and then to a vacuum line. The sample and thermocouple were placed in a manner identical with that in the experiments in which nitrogen was used. The end of the furnace opposite the ground glass joint was closed with a glass wool plug. The pressure inside the vacuum line, as measured by a McLeod gauge, was 5–10 μ .

The optimum temperature for the preparation of a given compound was taken to be near the center of the range defined by the temperature at which bipyridine was observed to condense at the cooler end of the Pyrex tube and the temperature at which another compound was observed to form, as generally indicated by a distinct color change in the sample. In instances where this range was large (30–100°), the exact temperature was not critical.

In preliminary experiments, the completion of a given reaction was ascertained by weighing the sample and boat and heating until constant weight was obtained. However, in almost every case, reaction was accompanied by a readily observable color change. Where this occurred, the reaction could be assumed to be complete when heating was continued for about 2 hr. after no further color change was apparent.

Results and Discussion

The results of the controlled thermal decomposition studies are outlined in the following flow charts, which give the empirical formulas and the colors of the compounds produced and indicate the conditions under which each was obtained. Heating times varied from 6–8 hr. in some instances to as much as 30–36 hr. in others.

(8) F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, *J. Am. Chem. Soc.*, **83**, 4157 (1961).

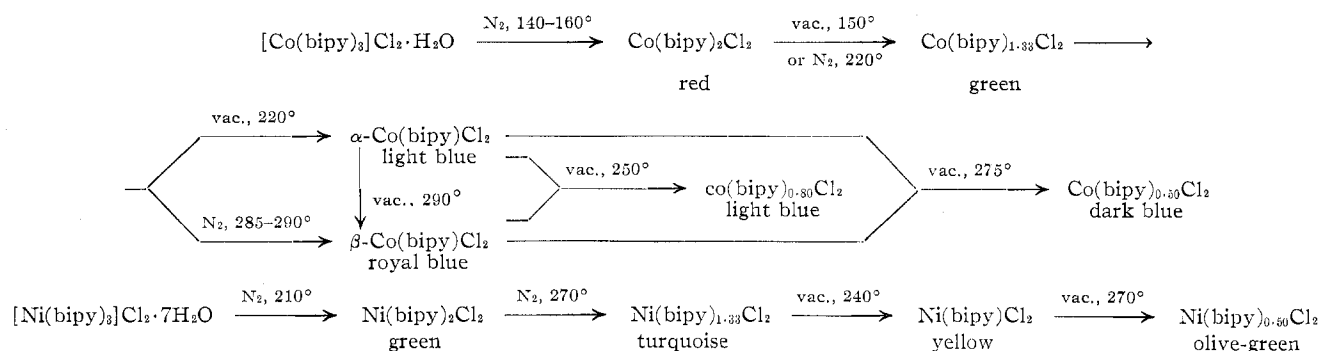


TABLE I
MAGNETIC MOMENTS AND ANALYTICAL AND WEIGHT LOSS DATA

Compound	μ_{eff}^a 24-25°	Metal, %		Cl, %		No. indep. prep. run	Source	Weight loss ^b	
		Calcd.	Found	Calcd.	Found			Calcd.	Found
Co(bipy) ₂ Cl ₂	4.92	13.33	13.30	16.03	15.90	2			
Co(bipy) _{1.33} Cl ₂	4.91	17.43	17.48	20.97	20.86	2	Co(bipy) ₂ Cl ₂	0.667	0.672
α-Co(bipy) ₂ Cl ₂	5.10	20.61	20.71	24.79	24.86	1	Co(bipy) _{1.33} Cl ₂	0.333	0.344
			20.50	24.62	2	Co(bipy) ₂ Cl ₂	1.000	1.015	
β-Co(bipy) ₂ Cl ₂	4.93		20.64		24.79	2	Co(bipy) _{1.33} Cl ₂	0.333	0.341
"Green Co(bipy) ₂ Cl ₂ "	4.33		20.47		24.44	2			
Co(bipy) _{0.80} Cl ₂	5.15	23.13	23.27	27.82	27.70	1	β-Co(bipy) ₂ Cl ₂	0.200	0.217
			23.03	27.62	1	α-Co(bipy) ₂ Cl ₂		0.229	
Co(bipy) _{0.50} Cl ₂	5.24	28.34	28.45	34.10	33.55	1	α-Co(bipy) ₂ Cl ₂	0.500	0.565
			28.24	33.71	1	β-Co(bipy) ₂ Cl ₂	0.500	0.565	
Ni(bipy) ₂ Cl ₂	3.20	13.28	13.16	16.04	15.93	1			
Ni(bipy) _{1.33} Cl ₂	3.46	17.37	17.23	21.00	20.85	2	Ni(bipy) ₂ Cl ₂	0.667	0.672
Ni(bipy)Cl ₂	3.38	20.54	20.53	24.81	24.73	3	Ni(bipy) ₂ Cl ₂	1.000	1.024
Ni(bipy) _{0.50} Cl ₂	3.70	28.25	28.28	34.13	33.92	2	Ni(bipy) ₂ Cl ₂	0.500	0.490

^a In Bohr magnetons. ^b Expressed as moles of 2,2'-bipyridine (bipy) lost per gram atomic weight of metal in producing the compound from the source indicated.

In Table I the percentages of metal and chloride found in each compound are given (each set of percentages represents the results of replicate analyses on a separate preparation), together with the loss in weight which occurred in the preparation of a given compound from one of the earlier compounds in the series. The effective magnetic moment of the metal ion, computed from the room-temperature magnetic susceptibilities, also is included in the table.

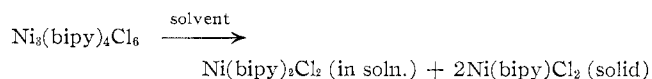
The empirical formulas which have been assigned to the various products in the flow charts and in Table I appear to be well substantiated by the analytical results. The weight loss data, although less reliable (because of significant volatilization and probable mechanical loss from necessary crushing of material during the heating period in some instances), provide corroborative evidence for the formulations.

Further characterization of these materials was afforded by electronic absorption spectra, X-ray diffraction patterns, magnetic susceptibilities, and electrolytic conductance. The results of these studies and their interpretation in terms of structure are discussed below in connection with the specific types of compounds produced. Before proceeding with this discussion, some general observations on the solution behavior of these substances may be reported.

All of the compounds were found to be insoluble in benzene and in carbon tetrachloride. All are readily soluble (with immediate solvation) in water and in

N,N-dimethylformamide. All are soluble in ethanol, although those containing lower proportions of bipyridine dissolve more slowly than the others. With the exception of Ni(bipy)Cl₂ and Ni(bipy)_{0.50}Cl₂ (both rather insoluble), all are sparingly soluble in acetonitrile, nitromethane, and nitrobenzene—the solubilities appearing to decrease in that order.

In both nitromethane and acetonitrile the compound of empirical formula Ni(bipy)_{1.33}Cl₂ underwent decomposition corresponding to the equation



Identification of the products of this reaction was made by means of the absorption spectra, and the relative proportion in which they were formed was established from the weight of the solid and the absorbance of the Ni(bipy)₂Cl₂ in acetonitrile solution.

Co(bipy)₂Cl₂ and Ni(bipy)₂Cl₂.—Harris and McKenzie² found Ni(bipy)₂Cl₂ to be essentially a nonelectrolyte in nitrobenzene and nitromethane solutions, and proposed an octahedral structure for it. The absorption spectrum, shown in Fig. 1, exhibits a peak at 622 mμ and a broad maximum at about 1050 mμ and is consistent with this structure.⁹ In the present work the molar conductance of Co(bipy)₂Cl₂ at 0.001 M concentration in nitrobenzene was found to be only 2.85, whereas that of tetraphenylarsonium chloride was

(9) C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 1362 (1955); **10**, 887 (1956).

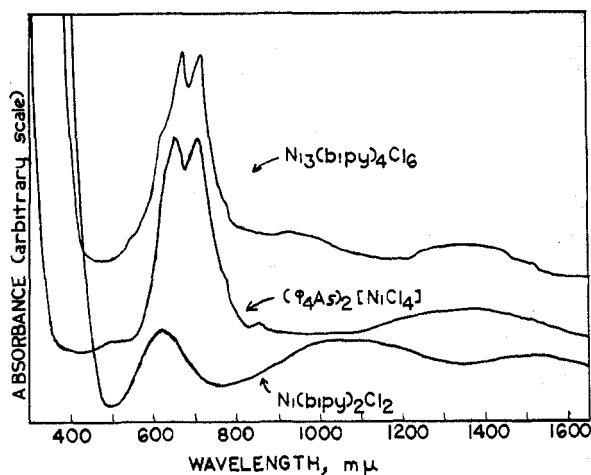


Fig. 1.—Absorption spectra of nickel complexes in Nujol mulls.

28.4. At the same concentration in nitromethane, the molar conductance of the cobalt compound was 37, in contrast to 106.1 for tetramethylammonium chloride. In view of this behavior, $\text{Co}(\text{bipy})_2\text{Cl}_2$ may also be regarded as a nonelectrolyte and is presumed to have octahedral coordination of the metal ion. The absorption spectrum, shown in Fig. 2, supports this conclusion.

It may be mentioned that the X-ray diffraction patterns¹⁰ show $\text{Co}(\text{bipy})_2\text{Cl}_2$ and $\text{Ni}(\text{bipy})_2\text{Cl}_2$ not to be isomorphous.

$\text{Co}(\text{bipy})_{1.33}\text{Cl}_2$ and $\text{Ni}(\text{bipy})_{1.33}\text{Cl}_2$.—The X-ray diffraction patterns showed these two compounds to be isomorphous and demonstrated clearly that they are not mixtures of their respective precursors, $\text{M}(\text{bipy})_2\text{Cl}_2$, with the products, $\text{M}(\text{bipy})\text{Cl}_2$, which result from the next step in the thermal decomposition.

In addition to being produced by thermal decomposition of $\text{Co}(\text{bipy})_2\text{Cl}_2$, the cobalt compound was also obtained as a pale green insoluble powder when acetone solutions of anhydrous cobalt chloride and 2,2'-bipyridine were mixed in stoichiometric proportions.

The absorption spectra of the $\text{M}(\text{bipy})_{1.33}\text{Cl}_2$ compounds exhibit features which are characteristic of both octahedral coordination and tetrahedral coordination of the metal. This is clearly evident in Fig. 2, which shows a comparison of the spectrum of $\text{Co}(\text{bipy})_{1.33}\text{Cl}_2$ with that of octahedrally-coordinated $\text{Co}(\text{bipy})_2\text{Cl}_2$ and that of $[(\text{C}_6\text{H}_5)_4\text{As}][\text{CoCl}_4]$, in which the cobalt is known to be tetrahedrally coordinated. A similar comparison of the spectrum of $\text{Ni}(\text{bipy})_{1.33}\text{Cl}_2$ with the spectra of $\text{Ni}(\text{bipy})_2\text{Cl}_2$ and $[(\text{C}_6\text{H}_5)_4\text{As}][\text{NiCl}_4]$, shown in Fig. 1, leaves little room for doubt that this compound, too, contains both octahedrally- and tetrahedrally-coordinated nickel.

To satisfy both the stoichiometric and the stereochemical requirements, one structure that suggests itself is a trinuclear unit, formulated $\text{M}_3(\text{bipy})_4\text{Cl}_6$, consisting of an MCl_4 tetrahedron sharing two of its chlorides with two separate $\text{M}(\text{bipy})_2\text{Cl}_2$ octahedra. An-

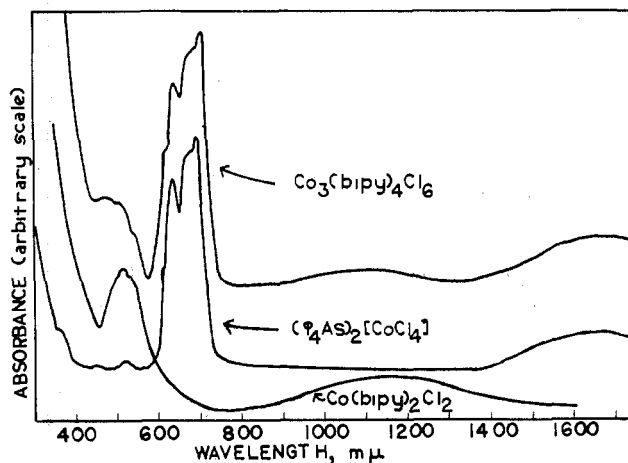


Fig. 2.—Spectra from Nujol mulls.

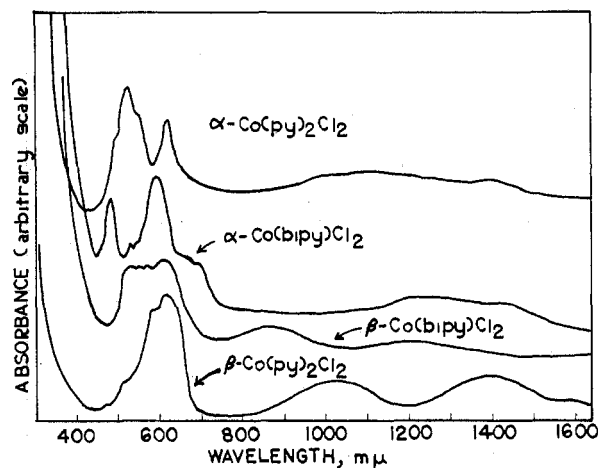


Fig. 3.—Spectra from Nujol mulls.

other possibility would be an ionic compound containing a dinuclear cation, $[(\text{bipy})_2\text{MCl}_2\text{M}(\text{bipy})_2]^{2+}$, and the tetrachlorometallate anion, MCl_4^{2-} . Choice between these structures might appear to be simply made from conductance measurements. However, low solubility and reactions of the type described earlier for $\text{Ni}_3(\text{bipy})_4\text{Cl}_6$ in acetonitrile and nitromethane introduce complications. Although the structures of these compounds cannot be more precisely pinpointed at present, there can be little question of the presence of both octahedrally- and tetrahedrally-coordinated metals in them. Additional support for this feature is provided by the magnetic moments.

If the intra- and intermolecular magnetic interactions are sufficiently small so that a polynuclear complex of this kind behaves magnetically as though it were a mixture of mononuclear species (obeying the Wiedemann mixture law), it can be shown that the polynuclear complex should then have a magnetic moment (per metal atom) which is equal to the root-mean-square of the magnetic moments of the species in the molecule

$$\mu_c = \sqrt{\left(\sum_i n_i \mu_i^2\right) / N}$$

where N is the number of nuclei in the complex, of

(10) For a table of d -values and relative intensities for these and the other compounds described, see R. H. Lee, Ph.D. thesis, University of Kansas, 1964.

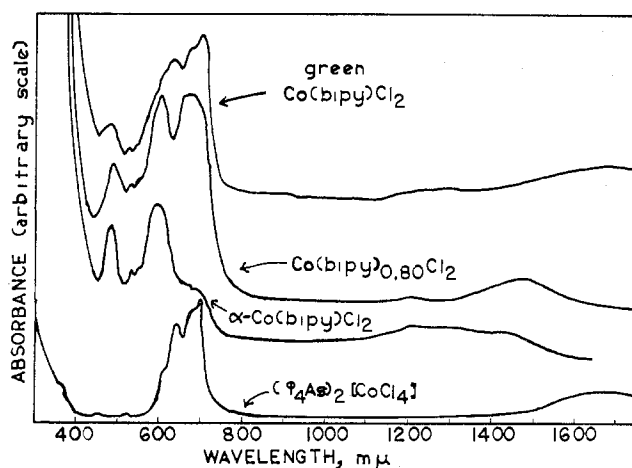


Fig. 4.—Spectra of Nujol mull preparations.

which n_i are of species i , possessing a magnetic moment μ_i .

Calculation of the expected magnetic moments in this manner gives for $\text{Co}_3(\text{bipy})_4\text{Cl}_6$, 4.85 B.M.; for $\text{Ni}_3(\text{bipy})_4\text{Cl}_6$, 3.44 B.M. The observed values (Table I) are, respectively, 4.91 and 3.46 B.M. The magnetic moments of the $\text{M}_3(\text{bipy})_4\text{Cl}_6$ compounds are thus quite consistent with either of the proposed structures. In calculating the expected moments, the following complexes and corresponding moments (in Bohr magnetons) were used: $\text{Co}(\text{bipy})_2\text{Cl}_2$, 4.92 (this work); CoCl_4^{2-} , 4.69¹¹; $\text{Ni}(\text{bipy})_2\text{Cl}_2$, 3.20 (this work); NiCl_4^{2-} , 3.88.¹¹

The Compounds $\text{M}(\text{bipy})\text{Cl}_2$.—It is especially interesting that two forms of $\text{Co}(\text{bipy})\text{Cl}_2$ have been obtained in the present work, in analogy with the two modifications of the bispyridine complex, $\text{Co}(\text{py})_2\text{Cl}_2$, which have long been known, and for which structures have been established.

The light blue $\text{Co}(\text{bipy})\text{Cl}_2$ shows an absorption spectrum which resembles that of the violet $\alpha\text{-Co}(\text{py})_2\text{Cl}_2$ isomer, as can be seen in Fig. 3. On the other hand, the spectrum of the royal blue monobipyridine product is distinctly different from these, but is rather similar to that of the blue $\beta\text{-Co}(\text{py})_2\text{Cl}_2$. The designation of the respective bipyridine compounds in this paper as α - and β - has been made on the basis of these similarities.

X-Ray structural studies¹² on $\alpha\text{-Co}(\text{py})_2\text{Cl}_2$ have shown the crystal to consist of polymeric chains of octahedra, in which two chlorides serve as bridging groups between two cobalt atoms. The two pyridine nitrogens are coordinated *trans* to each other. It seems very likely that the light blue bipyridine compound designated $\alpha\text{-Co}(\text{bipy})\text{Cl}_2$ also possesses a polymeric octahedrally-coordinated structure. Here, of course, the two nitrogen atoms must occupy *cis* positions, so the chains of octahedra would differ in detail from those of the pyridine analog. Besides the evidence supplied by the absorption spectrum, the high magnetic moment of 5.10 B.M. lends support to the octahedral structure,

since it lies in the range (4.8–5.6) commonly associated with octahedral spin-free cobalt(II) complexes.^{13,14}

The similarity of the absorption spectrum of $\beta\text{-Co}(\text{bipy})\text{Cl}_2$ to that of $\beta\text{-Co}(\text{py})_2\text{Cl}_2$ (Fig. 3) strongly suggests that the first compound probably has the same structure as does the pyridine analog, which has been shown¹⁵ by X-ray studies to be tetrahedral. Supporting evidence for this structure comes from the low molar conductance of $\beta\text{-Co}(\text{bipy})\text{Cl}_2$ in nitromethane (37.0 at 0.001 *M* concentration), which indicates that it may be regarded as essentially a nonelectrolyte. Certainly the possibility of formulating the compound as $[\text{Co}(\text{bipy})_2][\text{CoCl}_4]$ is ruled out. The magnetic moment (4.93 B.M.) is somewhat higher than the values usually found¹³ for tetrahedrally-coordinated cobalt(II), but is distinctly lower than that for the α - form.

The spectrum of $\beta\text{-Co}(\text{bipy})\text{Cl}_2$ in nitromethane solution is very similar to that exhibited by the solid in Nujol mull. When $\alpha\text{-Co}(\text{bipy})\text{Cl}_2$ is dissolved in nitromethane, however, it changes to the β - form, as indicated by the spectrum. Similar behavior has been observed with the analogous α - and $\beta\text{-Co}(\text{py})_2\text{Cl}_2$.¹⁶

Prolonged heating of either α - or $\beta\text{-Co}(\text{bipy})\text{Cl}_2$ causes some volatilization (more readily with the β - form), and the solid which condenses in either instance is the β - form. This observation and the behavior on dissolution in nitromethane are consistent with the view that the α - form is polymeric, the β - form monomeric.

A green product, presumably the material described by Yamasaki,⁸ and having very nearly the same composition as the compounds just described, was obtained when aqueous solutions of either the α - or $\beta\text{-Co}(\text{bipy})\text{Cl}_2$ were evaporated to dryness and the residue was dried at about 150°. The absorption spectrum (Fig. 4) indicates the presence of both the tetrahedral CoCl_4 unit and an octahedral unit. The corresponding peaks in this spectrum, although showing some variation in height relative to each other in different preparations, appear to be of roughly the same intensity, indicating the proportion of tetrahedral units to be low, since the molar absorbances characteristic of tetrahedral coordination are typically larger by a factor of the order of 10² than those characteristic of octahedral coordination. In the X-ray diffraction pattern, many of the strongest lines which characterized $\alpha\text{-Co}(\text{bipy})\text{Cl}_2$ appear, along with a number of other lines which have not been identified. From the variability in composition and in the spectrum, together with the X-ray data, it seems probable that this material is a mixture made up predominantly of $\alpha\text{-Co}(\text{bipy})\text{Cl}_2$, but containing some hydrolytic products in which small amounts of CoCl_4^{2-} are present.

Comparison of the X-ray diffraction pattern of $\text{Ni}(\text{bipy})\text{Cl}_2$ with the patterns of the corresponding cobalt compounds shows the nickel compound to be isostruc-

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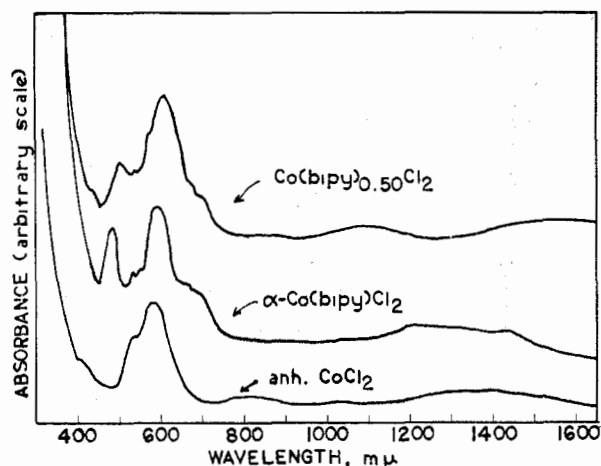


Fig. 5.—Spectra from Nujol mulls.

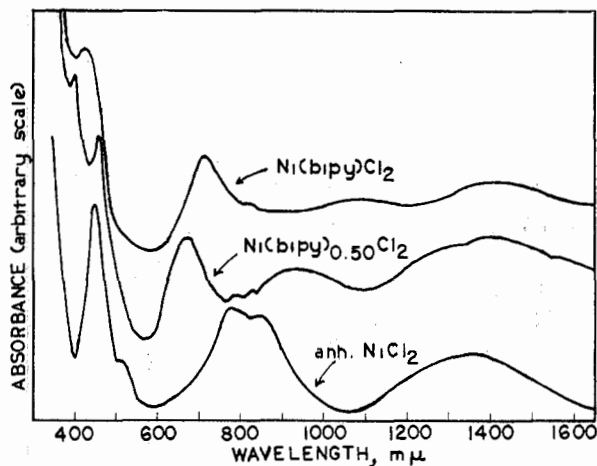


Fig. 6.—Spectra of Nujol mull preparations

tural with $\alpha\text{-Co(bipy)Cl}_2$. It must be presumed, therefore, to have a polymeric octahedral structure also. Confirmation is provided by the close similarity between the principal features of the absorption spectrum of Ni(bipy)Cl_2 (Fig. 6) and those reported¹⁷ for $\text{Ni(py)}_2\text{Cl}_2$, which has been shown¹⁸ to be isostructural with the polymeric octahedrally-coordinated $\alpha\text{-Co(py)}_2\text{Cl}_2$. Moreover, the magnetic moment of Ni(bipy)Cl_2 , 3.38 B.M., is almost identical with that of the pyridine analog (3.37), and is about that expected¹⁴ for octahedrally-coordinated nickel(II).

$\text{Co(bipy)}_{0.80}\text{Cl}_2$.—The absorption spectrum of this compound, shown in Fig. 4, indicates the probable presence of both octahedral Co(bipy)Cl_4 and tetrahedral CoCl_4 groups. However, any structure, embodying these features and conforming to the stoichiometric requirements, which might be proposed at present would be highly speculative in view of the limited amount of evidence available.

$\text{Co(bipy)}_{0.50}\text{Cl}_2$ and $\text{Ni(bipy)}_{0.50}\text{Cl}_2$.—The X-ray diffraction patterns of these compounds show them to be isostructural. The absorption spectra of the two compounds shown, respectively, in Fig. 5 and 6, exhibit features which are characteristic of the polymeric octahedral M(bipy)Cl_2 compounds and also features characteristic of the anhydrous MCl_2 solid compounds, which consist of layers of MCl_6 octahedra.¹⁹ However, the X-ray diffraction patterns show that M(bipy)Cl_2 and MCl_2 are not present as such in these materials, which, therefore, cannot be simple mixtures of the two. The room-temperature magnetic moments offer little help here. That of $\text{Co(bipy)}_{0.50}\text{Cl}_2$ (5.24 B.M.) is

reasonable for octahedral coordination, that of $\text{Ni(bipy)}_{0.50}\text{Cl}_2$ (3.70) is distinctly higher than would be expected.

It is possible to envision a structure which might be formed from two adjacent chains of M(bipy)Cl_2 octahedra through the loss of one bipyridine molecule for each two metal atoms, accompanied by lateral condensation of the two chains, with pairs of chlorides serving as bridge groups. The resultant "double chain" would have two types of metal atoms in it in equal numbers: one surrounded by four chlorides and one bipyridine (as in $\alpha\text{-Co(bipy)Cl}_2$ and Ni(bipy)Cl_2), the other surrounded by six chlorides (as in MCl_2). Further loss of bipyridine, accompanied by lateral "fusion" of the chains, would appear to lead very simply to the MCl_2 structure. At temperatures necessary to effect this change, however, it is probable that extensive decomposition of the organic ligand might occur.⁴

Although elucidation of the detailed structures of the compounds discussed in this paper must await X-ray studies on single crystals, the principal stereochemical features which they possess appear now to be established. Among the compounds thus characterized in this work were some which have been previously prepared and the following compounds, which do not appear to have been previously reported: $\text{Co(bipy)}_2\text{Cl}_2$, $\text{Co}_3(\text{bipy})_4\text{Cl}_6$ and $\text{Ni}_3(\text{bipy})_4\text{Cl}_6$, $\text{Co(bipy)}_{0.80}\text{Cl}_2$, and $\text{Ni(bipy)}_{0.50}\text{Cl}_2$. It may be mentioned that the chloride analog of the compound $\text{Ni(bipy)}_{1.50}\text{Br}_2$ prepared by Dhar and Basolo⁶ was not obtained in the present investigation.

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