Atti Accademia Nazionale dei Lincei

Classe Scienze Fisiche Matematiche Naturali

Rendiconti

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The preparation and characterization of some bis (α, α'-dipyridyl)cobalt(III) complexes

Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti, Serie 8, Vol. **39** (1965), n.5, p. 310–316.

Accademia Nazionale dei Lincei

<http://www.bdim.eu/item?id=RLINA_1965_8_39_5_310_0>

Chimica. — *The preparation and characterization of some bis (α, α'-dipyridyl)cobalt(III) complexes* (*). Nota di Ferruccio Aprile e Federico Maspero, presentata (**) dal Corrisp. G. Sartori.

INTRODUCTION.

Complex ions of the formula Co $dipy_2X_2^+$ (dipy = α, α'-dipyridyl) and their u.v. and visible spectra have been known for many years [1, 2, 3, 4].

In a previous paper [5] we have pointed out the existence of some inherent difficulties in the preparation of compounds of that type, due to the nature of the chelating agent.

In view of future studies on reaction mechanisms, in the present paper we report the synthesis of the perchlorates of some *cis*-bis (α, α'-dipyridyl) cobalt (III) complex ions including the carbonato, the diaquo, the aquo hydroxo, the diacetato and the aquo acetato.

EXPERIMENTAL.

Materials.—All chemicals were reagent-grade. *Cis*-[Co $dipy_2Cl_2$]Cl was prepared as described by Jaeger and Van Dijk [1].

[Co $dipy_2CO_3$]ClO_4. In order to obtain this perchlorate salt, the procedure of Jaeger and Van Dijk [1] was modified as follows. Ten grams of $CoSO_4 \cdot 7\ H_2O$ and 11.2 g of α, α'-dipyridyl were nearly completely dissolved in 300 ml of water. A stream of air passed through the yellow solution for five or six hours, until all dipyridyl was dissolved and the solution turned brown yellow. Sodium carbonate (7.5 g) was dissolved in 100 ml of water and added to the first solution; the mixture was evaporated on the steam bath until its volume was reduced to 50 ml and its colour turned pink. The solution was allowed to cool overnight, and a pink precipitate of [Co $dipy_2CO_3]_2SO_4$, containing cobalt(III) hydroxide as impurity, was obtained. This precipitate was placed in a sintered glass funnel and washed with ethanol until the washings were colourless. The solid was then dissolved with the minimum amount of water, leaving the insoluble cobalt(III) hydroxide on the sintered glass.

Solid $NaClO_4$ was added to the solution soon after, and a pink precipitate appeared. Yield: 12%. (Found: Co, 11.4; calc. for [Co $dipy_2CO_3$]ClO_4: Co, 11.10%).

Cis-*[Co $dipy_2(H_2O)_2$]$(ClO_4)_3$.* Ten grams of [Co $dipy_2CO_3$]ClO_4 were mixed with 200 ml of water and 70 ml of 1 M $HClO_4$. The mixture was evaporated on the steam bath until 50 ml. A red-scarlet precipitate was obtained on cooling at room temperature. The precipitate was filtered on a sintered glass funnel and washed with absolute ethanol until elimination of $HClO_4$ in the washings. Yield: 70%. (Found: Co, 8.4; C, 34.1; H, 3.27; Calc. for [Co $dipy_2(H_2O)_2]_2(ClO_4)_3$: Co, 8.35%; C, 34.04%; H, 2.87%).

(*) Lavoro eseguito presso il Centro di Chimica dei Composti di Coordinazione del C.N.R. e l'Istituto di Chimica Generale dell'Università di Roma. La presente Nota è la Parte V della serie: Struttura e reattività nei complessi ottaedrici.

(**) Nella seduta del 13 novembre 1965.

Red-scarlet crystalline powder, readily soluble in water. Two equivalents of NaOH exactly neutralize one mole of the complex salt.

Cis–$[Co\ dipy_2(OCOCH_3)_2]ClO_4$. Three grams of $[Co\ dipy_2CO_3]ClO_4$ were treated with 100 ml of water and 40 ml of acetic acid, and the resulting mixture was evaporated on the steam bath until it reduced to 50 ml. After cooling, the residual unreacted carbonate was filtered out. The red solution was then evaporated to dryness on the steam bath. The dry residue was collected and recrystallized from dry ethanol. Yield: 50%. (Found: Co, 10.1; C, 48.2; H, 3,83; Calc. for $[Co\ dipy_2(OCOCH_3)_2]ClO_4$: Co, 10.0%; C,48.8%; H, 3.75%).

Red-purple powder, readily soluble in water, soluble in methanol and ethanol.

Cis–$[Co\ dipy_2(H_2O)(OCOCH_3)](ClO_4)_2$. Three grams of $[Co\ dipy_2(OCOCH_3)_2]ClO_4$ were treated with diluted perchloric acid so to give a solution $4\cdot 10^{-2}$ M in Co $dipy_2(OCOCH_3)_2^+$ and $5\cdot 10^{-2}$ M in $HClO_4$. The flask was immersed in a thermostate at 35° C for 25 minutes, then rapidly cooled. Solid $NaClO_4$ was added until a pink precipitate appeared. The precipitate was collected on a sintered glass filter and washed with a pH = 3 solution, then with ethanol and ether. Yield: 80%. (Found: C, 40.9; H, 3.38; Cl, 10.9; Calc. for $(Co\ dypy_2(H_2O)(OCOCH_3)](ClO_4)_2$: C, 40.8%; H, 3.25%; Cl, 10.9%).

Cis–$[Co\ dipy_2(H_2O)(OH)](ClO_4)_2$. The diaquo complex (3.2 g) was dissolved in 400 ml of water, and $NaClO_4$ was added up to 0.5 M ionic strenght. One equivalent of sodium hydroxide was then added (4.5 ml of 1 M solution). In a short time, a pink precipitate began to form. The product was collected and washed with absolute ethanol. Yield: 85%. (Found: C, 40.6; H, 3.49; Calc. for $[Co\ dipy_2(H_2O)(OH)](ClO_4)_2$: C, 40.0%; H, 3.16%).

Pink powder, fairly soluble in water.

Analysis.—The percentage determination of Co was performed as described by Vogel [6]. The microanalyses of C, H, Cl were made by A. Bernhardt, Mülheim/R.

Spectrophotometric measurements.—All spectrophotometric measurements were carried out using a Beckman model D.U. quartz spectrophotometer provided with a thermostatic cell compartment.

Solutions of the complexes were about 0.003 M for measurements in the region of 350 to 700 mμ, and 0.00003 M in the region of 220 to 350 mμ.

Measurements of acid dissociation constants.—Acid dissociation constants were determined potentiometrically using glass and satd. calomel electrodes, the latter being conveniently prepared in the laboratory. A shielded pH–meter (Jonosis, SIS, Milano; precision = = 1/100 pH unit) was used. The system was standardized with a pH = 7 Beckman 3501 buffer.

In each experiment a small excess of sodium hydroxide was added to the solution 1 to $12\cdot 10^{-3}$ M of Co $dipy_2(H_2O)_2^{+3}$, the ionic strength being adjusted at the desired value with $NaClO_4$; the resulting solution was back titrated using perchloric acid at a concentration 100 times as high as that of the dihydroxo complex. During the measurements a CO_2–free nitrogen stream was allowed to pass through the solution.

RESULTS AND DISCUSSION.

Preparation of the complexes.

We first tried to prepare *cis*–Co $dipy_2(OCOCH_3)_2^+$ by the reaction of silver acetate with *cis*–$[Co\ dipy_2Cl_2]Cl$; this method, however, was unsuccessful. The diacetato complex was obtained by the reaction of Co $dipy_2CO_3^+$ with acetic acid. The carbonato complex ion had been known for long [1], but we have been using a different method of synthesis, based on the oxidation of a mixture of a cobalt(II) salt and α, α′–dipyridyl by the air, followed by heating of the oxidized solution in the presence of Na_2CO_3.

TABLE I.

Spectral data for some dipy-cobalt(III) complexes in aqueous solutions and for free α, α'-dipyridyl.

Compounds	I λ (mμ)	 lg ε	IIIa λ (mμ)	 lg ε	IIIb λ (mμ)	 lg ε	IIIc λ (mμ)	 lg ε	IIId λ (mμ)	 lg ε	Refs.
cis–Co $\text{dipy}_2(\text{OAc})_2^+$	509	2.08	—	—	305	4.30	(248)	(4.55)	222	4.68	
cis–Co $\text{dipy}_2(\text{H}_2\text{O})_2^{+3}$	490	1.76	315	4.33	305	4.38	(245)	(4.45)	220	4.58	
a) *cis*–Co $\text{dipy}_2(\text{OH})_2^+$	510	1.86	—	—	310	4.32	(245)	(4.50)	215	4.67	
cis–Co $\text{dipy}_2\text{H}_2\text{O OAc}^{+2}$ . . .	495	1.92	—	—	305	4.29	(245)	(4.40)	220	4.66	
b) *cis*–Co $\text{dipy}_2\text{H}_2\text{O OH}^{+2}$ . . .	505	1.85	plateau		307	4.34	(245)	(4.45)	220	4.70	
Co $\text{dipy}_2\text{CO}_3^+$	510	2.00	—	—	303	4.45	—	—	—	—	
Co dipy_3^{+3}	448	1.87	315	4.97	304	4.48	(245)	(4.65)	222	4.91	[2]
dipy (in H_2O)	—	—	—	—	280	4.12	232	4.04	—	—	[2, 3]
dipy (in 1 M HCl)	—	—	—	—	303	4.13	243	3 82	—	—	[2]
dipy (in hexane)	—	—	—	—	280	4.12	244	4.03	235	4.03	[3]

NOTES: a) Compound not obtained in the solid form, but surely present in the solution. b) Identical to diaquo in a pH = 5 solution.

All the other complexes were obtained by stepwise or overall hydrolysis of the diacetato or of the carbonato complex under controlled conditions.

Only the synthesis of *cis* isomers of this series has been successful. We failed to obtain the *trans*–diacetato complex by *cis*–to–*trans* isomerization in protic as well as aprotic solvents (i.e.: water, methanol, ethanol, propanol, ethylene glicol, acetone, dimethylformamide, tetrahydrofuran, dimethylsulfoxide, acetonitrile); in some cases, after several days at 70° C, the solutions became yellowish, and their absorption spectra were very similar to Co dipy$_3^{+3}$. Also, no isomerization has ever been observed with *cis*–Co dipy$_2$(H$_2$O)(OCOCH$_3$)$^{+2}$.

In the literature other examples with related compounds are reported, whereby *trans* isomers could not be obtained. Thus, Ablov could not synthetize *trans*–Co phen$_2$Cl$_2^+$ ion [7], and Livingstone could not get complexes of the type *trans*–Pd dipy$_2$X$_2$ or *trans*–Pt dipy$_2$X$_2^+$ [8]. In such cases, steric hindrance effects were held responsible for these findings.

Similarly, it seems to be very difficult to obtain Co dipy$_2$X$_2^{+n}$ in the *trans* form. The early report of *trans*–Co dipy$_2$Cl$_2^+$ by Jaeger and Van Dijk [1] has been recently disproved [5].

Absorption spectra and characterization.—The visible and u.v. spectra of the compounds herein reported are recorded in Table I, together with the bands of some other compounds of interest for a comparison with them.

The α , α'–dipyridyl coordination can be shown by comparing the u.v. bands of the complex ions with the ones relative to the free ligand, because the u.v. bands of octahedral complexes are to be attributed to ligand → metal electron transfer transitions [9].

The bathocromic shift of the band IIIb of α , α'–dipyridyl in HCl solutions has been attributed to a change in the electronic configuration due to a hydrogen bond N—H—N, with a subsequent conversion to *cis* configuration of the molecule from the more stable *trans* configuration of the free base [10, 11]. Such a shift of the same band of the complexes compared with the one relative to free dipyridyl confirms that chelation occurs; the shift is similar to that found in the case of Co dipy$_3^{+3}$ by other Authors [2].

Co dipy$_3^{+3}$ and many other metal–dipy chelates show a split of the band III (IIIa and IIIb), while such a split cannot be observed in HCl solutions of α, α'–dipyridyl: this fact has been attributed [12] to the fine vibrational structure of the coordinated dipyridyl. We should point out that this is not the case for all the complexes herein reported, but only for *cis*–Co dipy$_2$(H$_2$O)$_2^{+3}$, while a plateau was observed in the case of *cis*–Co dipy$_2$(H$_2$O)(OH)$^{+2}$, and a single sharp peak in all other cases. Presumably, the resolution of such a split depends on the charge of the complex ion.

The configuration of the complexes can be assigned on the basis of the spectrum in the visible region. In fact, the latter can be attributed to the *d–d* transitions in the metal atom [9]. It is well known that the spectra of *cis*–CoA$_4$B$_2$, complexes are quite different from those of the corresponding *trans* isomers, and the examination of spectra in this region is considered as a reliable method of characterization [13].

Band II is screened by the absorption of the dipyridyl moiety.

On comparing band I relative to the compounds of our series with that of Co $dipy_2CO_3^+$ and of the corresponding complexes of the *cis*–bis(ethylenediamine) series, we can conclude that they are all *cis* isomers, on the basis of the values of log ε and of λ_{max}, that we have found similar for the two series [14, 15, 16, 17].

Unlike diaquo and dihydroxo complexes, there is some uncertainty in assigning the configuration of the aquo hydroxo complex using the same criteria. A better evidence that the *cis* $\rightleftarrows$ *trans* equilibrium is completely shifted to the left for this compound is given by the behaviour of the diaquo, aquo hydroxo and dihydroxo complexes. We have found that the absorption spectra of the three compounds change neither in the time interval of 24 hrs. nor in temperature interval of 5°–25° C. Samples of solution of the *cis*–diaquo complex were brought at a pH value corresponding to the existence of the aquo hydroxo complex; they were let stand for several days at room temperature, and then brought at a pH value corresponding to the diaquo or dihydroxo complexes. The absorption spectra of the two solutions were identical to those of the freshly prepared solutions of the same complexes. Keeping in mind that for Co $en_2H_2O\,OH^{+2}$ the *cis–trans* isomerization is very rapid [15], the above results indicate that no isomerization occurs in any case. Since it is possible to assign the configuration of diaquo and dihydroxo complexes on the basis of their spectra, we can conclude that, also in the case of Co $dipy_2H_2O\,OH^{+2}$, no *trans* isomer exists under the conditions of our experiments.

Acid dissociation constants of cis–*Co* $dipy_2(H_2O)_2^{+3}$.—The acid strength of this complex was determined according to the method described by Bjerrum and Rasmussen [15] and by Schwarzenbach [18]. pK_a values at zero ionic strength were obtained by extrapolation from the plots of lg K_a vs. $\sqrt{\mu}$ reported in fig. 1. In agreement with Brønsted's predictions [19], the slopes of the linear portion of the plots yielded the correct charge of the conjugated base $Zb = \frac{\partial pK_a}{\partial \sqrt{\mu}} = +1$ or $+2$, as expected for the species under investigation.

The pK_{a_1} and pK_{a_2} values were 3.3 and 5.5 respectively, at 25° C.

The range of ionic strength explored was 0 to 0.5 M; at $\mu > 0.5$ M a pink precipitate appeared during the titration, so that the determination was impracticable. Such a precipitate was then identified as *cis*–aquo hydroxo perchlorate.

The values found for the acid dissociation constants cannot be directly compared with the values found for the *cis*–Co $en_2(H_2O)^{+3}$ ion, because no measurements have been performed at $\mu = 1$ M, as had been done in that case [15]. However, since the observed values for both dissociation constants of *cis*–Co phen$_2$(H$_2$O)$_2^{+3}$ determined by Ablov et al. [20] are practically coincident in the slope lg $K_a = f(\sqrt{\mu})$ with the *cis*–Co dipy$_2$(H$_2$O)$_2^{+3}$, and almost independent on μ when $1 > \mu > 0.5$, we suppose such a trend to be valid also for the *cis*–Co dipy$_2$(H$_2$O)$_2^{+3}$. The assumption makes it possible

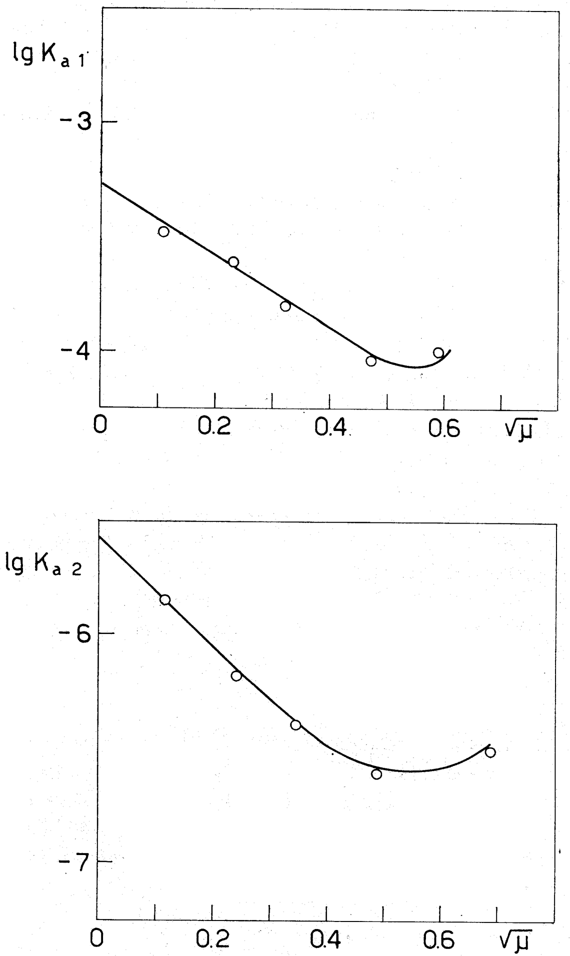

Fig. 1. – Correlation between the ionic strength and the acidity constants relative to *cis*–Co dipy$_2$(H$_2$O$_2$)$_2^{+3}$.

to compare the values of K_a relative to our system with those relative to *cis*–Co en$_2$(H$_2$O)$_2^{+3}$, and the comparison gives as a result that for both constants the bis(dipyridyl) complex is the stronger acid. This order of acid strength is in agreement with the expected polar effects of the ligands.

ACKNOWLEDGEMENTS. The Authors are greatly indebted to profs. V. Caglioti and G. Illuminati for helpful assistance in this work.

REFERENCES.

[1] F.M. JAEGER, J. A. VAN DIJK, «Z. anorg. allgem. Chem.», *227*, 273 (1936).

[2] J. CSÁSZÁR, E. HORVATH, «Acta Chim. Acad. Sci. Hung.», *24*, 259 (1960).

[3] K. YAMASAKI, «Bull. Chem. Soc. Japan», *13*, 538 (1938).

[4] F. BASOLO, R. E. MEEKER, R. G. PEARSON, «J. Inorg. Nucl. Chem.», *1*, 341 (1955).

[5] F. APRILE, M. LEDERER, F. MASPERO, «Atti Accad. Naz. Lincei» (Rend. Classe Sci. fis., mat. e nat.), ser. VIII, *36–1*, 70 (1964).

[6] A. I. VOGEL, *A text-book of quantitative inorganic analysis*, p. 524, Longmans, London (1961).

[7] A. V. ABLOV, «Russ. J. Inorg. Chem.», *6*, 157 (1961).

[8] S.E. LIVINGSTONE, B. WHEELAN, «Australian J. Chem.», *17*, 219 (1964).

[9] T.M. DUNN, in: J. LEWIS and R. G. WILKINS, *Modern Coordination Chemistry*, Interscience, New York (1960).

[10] R. H. LINNELL, A. KACZMARCZYK, «J. Phys. Chem.», *65*, 1196 (1961).

[11] KAZUO NAKAMOTO, «J. Phys. Chem.», *64*, 1420 (1960).

[12] KOZO SONE, P. KRUMHOLZ, H. STAMMREICH, «J. Am. Chem. Soc.», *77*, 777 (1955).

[13] R. G. WILKINS, M. J. WILLIAMS, in: J. LEWIS and R. G. WILKINS, *Modern Coordination Chemistry*, Interscience, New York (1960).

[14] M. LINHARD, M. WEIGEL, «Z. anorg. allgem. Chem.», *264*, 321 (1951).

[15] J. BJERRUM, S. E. RASMUSSEN, «Acta Chem. Scand.», *6*, 1265 (1952).

[16] Y. SHIMURA, R. TSUCHIDA, «Bull. Chem. Soc. Japan», *29*, 311 (1956).

[17] V. CARUNCHIO, G. ILLUMINATI, G. ORTAGGI, to be published.

[18] G. SCHWARZENBACH, in *Chimica Inorganica – IV Corso Estivo di Chimica*, Accademia Nazionale dei Lincei, Roma (1961).

[19] J. N. BRØNSTED, «Z. Physik. Chem.», *134*, 97 (1928).

[20] A. V. ABLOV, D.M. PALADE, «Russ. J. Inorg. Chem.», *6*, 306 (1961).

RIASSUNTO. — Sono stati sintetizzati i perclorati di una serie di ioni complessi del tipo *cis*-Co(III)dipy$_2$XY^{+n}, comprendente il carbonato, il diaquo, l'aquo idrosso, il diacetato e l'aquo acetato. Per la caratterizzazione di questi composti sono stati registrati gli spettri di assorbimento u.v. e nel visibile. Inoltre sono state determinate le due costanti di dissociazione acida del complesso diaquo. Vengono presi in esame i vari aspetti riguardanti la configurazione e le proprietà di questi composti.