Absorption Spectra of Co(III) Complexes. II. Redetermination of the Spectrochemical Series

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In the course of our studies on thec urve analyses of absorption spectra¹⁾, the absorption curves of many Co(III) complexes have been determined. In the present paper, experimental details will be given for the cobaltic ammine, oxalato, carbonato and amino-acido complexes. Moreover, the "spectrochemical series" will be redetermined on the basis of the new data.

Experimental

Absorption measurements were made in aqueous solutions by a Beckman DU spectrophotometer, or by a spectrograph with a sector photometer. The concentration of the solutions varied from 1.0×10^{-2} to 3.3×10^{-5} gram complex-ion per litre. All measurements were made at room temperature. The complex perchlorates were used to minimize interaction between the complex ion and anions. The complexes were analyzed for water of crystallization and for perchlorate ion²⁾.

The results of the measurements are shown in

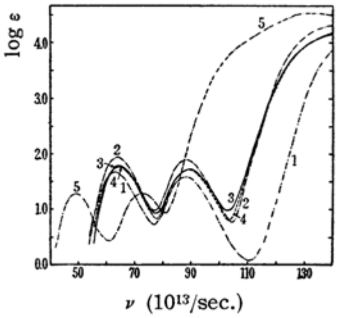

Fig. 1. Absorption curves of:
1, [Co $(NH_3)_6$] $(ClO_4)_3$;
2, [Co en_3] $(ClO_4)_3$;
3, *cis*-[Co en_2 $(NH_3)_2$] $(ClO_4)_3\cdot H_2O$;
4, ***trans***-[Co en_2 $(NH_3)_2$] $(ClO_4)_3\cdot H_2O$;
5, [Co $(O_6Mo_6O_{18}H_6)$] $(NH_4)]_3\cdot 7H_2O$.

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1) Part I of this series: Y. Shimura and R. Tsuchida, This Bulletin, **28**, 572 (1955).

2) M. Linhard and G. Stirn, *Z. anorg. Chem.*, **268**, 105 (1952).

Figs. 1-5. The numerical data for the first and the second absorption bands were previously reported[1].

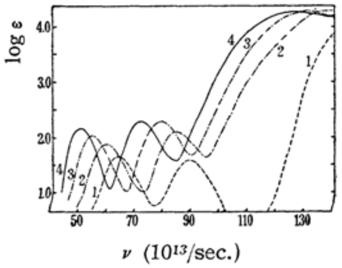

Fig. 2. Absorption curves of Co (III) ammine-oxalato series:
1, [Co $(NH_3)_6$] $(ClO_4)_3$;
2, [Co $(NH_3)_4$ ox] $ClO_4\cdot H_2O$;
3, [Co $(NH_3)_2$ ox_2] $NH_4\cdot H_2O$;
4, [Co ox_3] $K_3\cdot 3H_2O$.

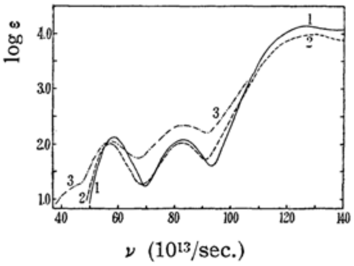

Fig. 3. Absorption curves of Co(III) carbonato complexes:
1, [Co en_2 CO_3] ClO_4;
2, [Co $(NH_3)_4$ CO_3] ClO_4;
3, [Co $(NH_3)_4$ CO_3] ClO_4 (solution after standing three hours at room temperature).

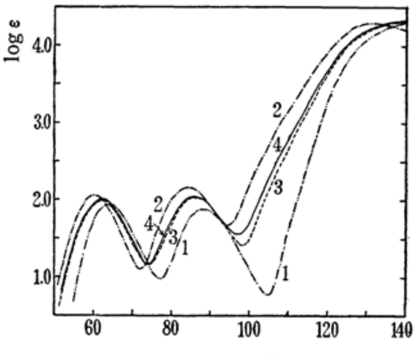

Fig. 4. Absorption curves of:
1, [Co en_3] $(ClO_4)_3$;
2, [Co en_2 ox] $Cl\cdot 3H_3O$;
3, [Co en_2 glycine'] $(ClO_4)_2$;
4, [Co en_2 leucine'] $(ClO_4)_2$.

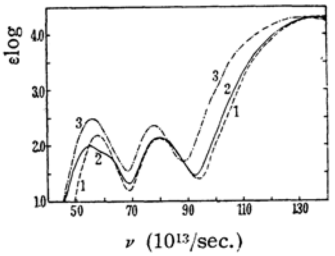

Fig. 5. Absorption curves of amino-acido complexes of Co(III);
1, β-[Co glycine'$_3$]$\cdot H_2O$;
2, α-[Co glycine'$_3$]$\cdot 2H_2O$;
3, [Co edta] $Na\cdot 4H_2O$.

Description of the Individual Complexes

α-[Co(glycine')$_3$]$\cdot 2H_2O$ and β-[Co(glycine')$_3$]$\cdot H_2O$.—For the preparations, the method of Ley and Winkler[3] was followed. The α-form has purple color and the β-form red. These two forms correspond to geometric isomers, *cis-cis* and *cis-trans* forms. The β-isomer was insoluble in water and the spectrum of the isomer was measured in 60% $HClO_4$. As will be seen in Fig. 5, the main difference between the curves of the two isomers occurred in the region of the first band: the first band of the β-form is normal but the α-form shows distinct indication of splitting of the first band. This splitting may be considered as a proof for the *cis-trans* structure of the α-form, since the similar splitting was reported for the first band of *trans*-[Co$(NH_3)_4(OCOCH_3)_2$] ClO_4 and not for the first band of the corresponding *cis* isomer[4].

[Co en_2glycine'] $(ClO_4)_2$ and [Co en_2 leucine'] $(ClO_4)_2$.—These perchlorates were prepared by adding concentrated aqueous solution of $NaClO_4$ and alcohol to the solutions of the corresponding chlorides[5]. They were twice recrystallized from water-alcohol mixture, and washed by alcohol and dried in air. The absorption curves of the two complexes have almost the same features.

[Co$(NH_3)_4CO_3$]ClO_4[6].—The tetrammine complex was unstable in aqueous solutions. The decomposition intermediates have more hyperchromic and more diffuse bands than the original tetrammine complex (see Fig. 3). The bisethylenedaimine complex was very stable in aqueous solutions

cis- and trans- [Co $en_2(NH_3)_2$] $(ClO_4)_3\cdot H_2O$.—These were precipitated from the concentrated

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[3] H. Ley and H. Winkler, *Ber.*, **42**, 3894 (1909); H.F. Holtzclaw, Jr. and D.P. Sheetz, *J. Am. Chem. Soc.*, **75**, 3053 (1953).

[4] M. Linhard and M. Weigel, *Z. anorg. Chem.*, **264**, 321 (1951).

[5] J. Meisenheimer, L. Angermann and H. Holsten, *Ann.*, **438**, 261 (1924); I. Lifschitz, *Rec. trav. chim.*, **58**, 785 (1939).

[6] M. Linhard and M. Weigel, *Z. anorg. Chem.*, **260**, 65 (1949).

solutions of the corresponding chlorides7) by addition of 60% $HClO_4$, and were recrystallized twice from water and dried in air. The freshly dried crystals were analyzed since they effloresced on exposure to the air.

$[Co(NH_3)_6](ClO_4)_3$, $[Co\ en_3](ClO_4)_3$, $[Co\ en_2CO_3]ClO_4$ $[Co\ en_2\ ox]Cl\cdot 3H_2O$, $NH_4[Co\ ox_2(NH_3)_2]\cdot H_2O$, $K_3[Co\ ox_3]\cdot 3H_2O$ and $Na[Co\ edta]\cdot 4H_2O$ were prepared essentially by the method described in literature.

Spectrochemical Series for the Ligands of Co (III) Complexes

The spectrochemical series represents the order of hypsochromic effects of ligands on the first or second absorption band of metallic complexes. During about the two decades which have elapsed since the first determination of the series by Tsuchida8), a great deal of new measurement has been made by many authors. Examining the data found in literature as well as in the author's measurements, revision of the series for the ligands of Co(III) complexes has been attempted.

In Table I to VI, the ligands have been arranged in the order of frequencies of the first bands of their comlexes.

Abbreviations and Conventions i) An unidentate ligand is designated by the full formula. The atom which is attached directly to the central cobalt atom takes precedence of the other atoms; for example, chromate ion, $OCrO_3^{=}$; unidentate oxalate ion, $OCOCO_2^{=}$.

TABLE I

PENTAMMINE SERIES, $[Co(NH_3)_5A]$

Ligand, A	First band ν (log ε)	Second band ν (log ε)	Ref.	Supplementary refs.
NO_2^-	65.5 (2.00)	(( ))	Linhard (1951)9)	10, 11, 16)
$SO_3^{=}$	63.6 (2.15)	(( ))	Kiss (1938)10)	17)
NH_3	62.9 (1.68)	88.3 (1.60)	12)	10, 11, 13, 14, 15)
OH_2	61.6 (1.62)	87.5 (1.62)	Kuroya (1950)11)	10, 15)
ONO^-	61.1 (1.86)	(( ))	Linhard (1955)18)	11, 16)
NCS^-	60.5 (2.24)	(( ))	19)	10, 18, 20, 21)
ONO_2^-	60.0 (1.77)	86.6 (1.77)	19)	10)
$OSO_3^{=}$	60.0 (1.70)		8)	
$OCHO^-$	59.7 (1.77)	85.3 (1.65)	Linhard (1951)4)	
OH^-	59.6 (1.80)	81.1 (1.85)	Kiss (1938)10)	
$OCOCH_3^-$	59.6 (1.82)	85.2 (1.70)	Linhard (1951)4)	
$OCONH_2^-$	59.4 (1.85)	84.9 (1.70)	Linhard (1951)4,22)	
$OCOCO_2^{=}$	59.2 (1.87)	(( ))	8)	17)
$OCO_2^{=}$	59.2 (1.92)	(( ))	Kiss (1938)10)	17)
$SSO_3^{=}$	58.8 (1.82)	(( ))	19)	10, 23)
F^-	58.4 (1.70)	84.8 (1.63)	Linhard (1951)22)	
N_3^-	57.8 (2.41)	(( ))	Linhard (1951)24)	
Cl^-	56.2 (1.71)	82.5 (1.72)	Linhard (1951)22)	10, 11, 14, 15)
$OCrO_3^-$	55.6 (2.14)	(( ))	8, 25)	17)
Br^-	54.7 (1.77)	(( ))	Linhard (1951)22)	
I^-	51.8 (1.90)	(( ))	Linhard (1951)22)	

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7) A. Werner, *Ann.*, **386**, 1 (1912); A. Werner, F. Bräunlich, E. Rogowina and C. Kreutzer, ibid., **351**, 65 (1907).

8) R. Tsuchida, This Bulletin, **13**, 388, 436 (1938).

9) M. Linhard and M. Weigel, *Z. anorg. Chem.*, **267**, 113 (1951).

10) A. Kiss and D. Czeglédy, *Z. anorg. Chem.*, **235**, 407 (1938).

11) H. Kuroya, *J. Inst. Polytech. Osaka City Uuiv.*, C **1**, No. 1, 29 (1950).

12) This paper.

13) M. Linhard, *Z. Elektrochem.*, **50**, 224 (1944).

14) H. Kuroya and R. Tsuchida, This Bulletin, **15**, 427 (1940).

15) R. Tsuchida, *J. Chem. Soc. Japan*, **59**, 731 (1938).

16) B. Adell, *Z. anorg. Chem.*, **271**, 49 (1952).

17) H. Yoneda and M. Kobayashi, *J. Chem. Soc. Japan*, **75**, 1192 (1954).

18) M. Linhard, H. Siebert and M. Weigel, *Z. anorg. Chem.*, **278**, 287 (1955).

19) Y. Shimura, unpublished data.

20) R. Tsuchida, *J. Chem. Soc. Japan*, **59**, 586 (1938).

21) Y. Shimura, *J. Am. Chem. Soc.*, **73**, 5079 (1951).

22) M. Linhard and M. Weigel, *Z. anorg. Chem.*, **266**, 49 (1951).

23) A. Kiss, G. Auer and E. Major, *Z. anorg. Chem.*, **246**, 28 (1941).

24) M. Linhard and M. Weigel, *Z. anorg. Chem.*, **267**, 121 (1951).

25) R. Tsuchida and M. Kobayashi, This Bulletin, **13**, 471 (1938).

TABLE II

Cis SERIES OF TETRAMMINE COMPLEXES

Ligand	First band ν (log ε)	Second band ν (log ε)	Ref.	Supplementary refs.
NO_2^-	67.5 (2.20)	(( ))	Linhard (1951)9)	11, 14, 26)
$SO_3^=$	65.9 (2.26)	(( ))	27)	
NH_3	62.9 (1.68)	88.3 (1.60)	12)	
OH_2	60.0 (1.40)	84.0 (1.49)	28)	10)
ONO^-	58.8	(( ))	Yalman53)	
ox	58.7 (1.91)	84.0 (2.11)	12)	10, 11, 14, 17)
ONO_2^-	58.5 (1.7)	85 (1.6)	19)	
$OCHO^-$	58.2 (1.94)	82.5 (1.69)	Linhard (1951)4)	
carb	57.4 (2.01)	82.6 (2.02)	12)	10, 11, 14)
$OCOCH_3^-$	57.3 (2.01)	82.0 (1.77)	Linhard (1951)4)	
F^-	57.3 (1.74)	81.9 (1.51)	Linhard (1952)29)	
N_3^-	55.7 (2.42)	(( ))	Linhard (1951)24)	

TABLE III

Cis SERIES OF BISETHYLENEDIAMINE COMPLEXES

Ligand	First band ν (log ε)	Second band ν (log ε)	Ref.	Supplementary refs.
NO_2^-	69.0 (2.26)	(( ))	Adell (1951)30)	14, 26)
$SO_3^=$	67.1 (2.35)	(( ))	19)	
ONO^-	65.9 (2.13)	(( ))	Adell (1951)30)	
NH_3	64.4 (1.79)	89.4 (1.74)	12)	26)
en	63.9 (1.94)	88.4 (1.90)	12)	
gly	61.3 (2.00)	86.4 (2.04)	12)	
NCS^-	61.1 (2.53)	(( ))	19)	21, 26)
OH_2	60.6 (1.85)	84.5 (1.82)	Basolo (1950)26)	32)
ox	60.1 (2.05)	84.3 (2.16)	12)	11, 14, 31)
$OCOC_2H_5^-$	59.4 (2.16)	82.7 (1.91)	Linhard (1951)4)	
carb	58.4 (2.13)	83.0 (2.09)	12)	14)
OH^-	58* (1.97)*	81* (2.01)*	Bjerrum (1952)32)	
Cl^-	55.9 (1.95)	76.6 (1.84)	Linhard (1952)29)	26)
Br^-	54.3 (2.04)	(( ))	Linhard (1952)29)	

TABLE IV

Trans SERIES OF TETRAMMINE COMPLEYXES

Ligand	First band		Second band ν (log ε)	Ref.	Supplementary refs.
	Ia ν (log ε)	Ib ν (log ε)			
NO_2^-	68.2 (2.37)		(( ))	Linhard (1951)9)	11, 14, 26, 43)
$SO_3^=$	66.6 (2.32)		(( ))	27)	
NH_3	62.9 (1.68)		88.3 (1.60)	12)	
OH_2	58.6		84.0	Yalman53)	
$OCOCH_3^-$	54.4 (1.76)	64* (1.37)*	82.1 (1.76)	Linhard (1951)4)	
N_3^-	52.8 (2.57)		(( ))	Linhard (1951)24)	
Cl^-	47.7 (1.63)	63.0 (1.38)	74.8 (1.54)	Linhard (1952)29)	28)

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26) F. Basolo, *J. Am. Chem. Soc.*, **72**, 4393 (1950).

27) Y. Shimura, This Bulletin, **25**, 46 (1952).

28) R. Tsuchida, This Bulletin, **11**, 721 (1936).

29) M. Linhard and M. Weigel, *Z. anorg. Chem.*, **271**, 101 (1952).

30) B. Adell, *Acta Chem. Scand.*, **5**, 54 (1951).

31) A. Mead, *Trans. Farad. Soc.*, **30**, 1052 (1934).

32) J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952).

TABLE V

Trans SERIES OF BISETHYLENEDIAMINE COMPLEXES

Ligand	First band		Second band ν (log ε)	Ref.	Supplementary refs.
	Ia ν (log ε)	Ib ν (log ε)			
NO_2^-	69.8 (2.27)		(( ))	Adell (1951)33)	
NH_3	64.2 (1.77)		89.2 (1.73)	12)	11, 14, 26)
NCS^-	59.4 (2.44)		(( ))	19)	21, 26)
ONO^-	58.3 (1.72)		(( ))	Adell (1951)33)	
$ONO_2^=$	58 (1.8)	66 (1.6)	85 (1.9)	19)	
OH^-	57* (1.72)*		79* (1.73)*	Bjerrum (1952)32)	
$OCOC_2H_5^-$	55.7 (1.73)	67* (1.40)*	84.1 (1.80)	Linhard (19514)	
OH_2	55* (1.52)*	68* (1.57)*	86* (1.73)*	Bjerrum (1952)32)	26)
$SSO_3^=$	54.9 (1.93)		(( ))	19)	23)
F^-	51.6 (1.35)	67.9 (1.49)	82.8 (1.67)	Linhard (1952)29)	
Cl^-	48.8 (1.58)	64.9 (1.41)	77.5 (1.68)	1)	26, 29)
Br^-	45.6 (1.73)	(( ))	(( ))	Linhard (1952)29)	
I^-	44.8	(( ))	(( ))	Ernsberger (1934)34)	

TABLE VI

COMPLEXES CONTAINING ONLY ONE SPECIES OF LIGAND

Complex Ion	First band ν (log ε)	Second band ν (log ε)	Ref.	Supplementary refs.
$[Co(CN)_6]^{3-}$	?	?		10, 23, 26)
$[Co(C_5H_5)_2]^+$	74* (2.38)*	99* (3.04)*	Wilkinson (1952)37)	
$[Co\ dg_3]$	(( ))	(( ))	Nakahara (1954)38)	
$[Co\ dip_3]^{3+}$	66.7	(( ))	Yamasaki (1940)39)	
$[Co\ phen_3]^{3+}$	66.5 (2.49)	(( ))	Yamasaki (1953)40)	
$[Co\ pn_3]^{3+}$	64.5 (1.95)		Mathieu (1936)41)	
$[Co\ dien_2]^{3+}$	64.2	88.0	Brigando (1953)42)	
$[Co\ en_3]^{3+}$	63.9 (1.94)	88.4 (1.90)	12)	10, 11, 13, 14, 31)
$[Co(NH_3)_6]^{3+}$	62.9 (1.68)	88.3 (1.60)	12)	10, 11, 13, 15)
$[Co(ONO)_6]^{3-}$	62.8 (2.41)	(( ))	Kuroya (1950)11)	10, 43)
β-$[Co\ gly_3]$	57.7 (2.20)	80.2 (2.14)	12)	
$[Co\ edta]^-$	55.9 (2.51)	78.1 (2.36)	12)	
$[Co\ acac_3]$	51.0 (2.04)	74.0 (2.47)	Sone (1948)44)	45)
$[Co\ ox_3]^{3-}$	49.7 (2.17)	70.9 (2.30)	12)	10, 31, 46, 47)
$[Co(O_6Mo_6O_{18}H_6)]^{3-}$	49.2 (1.29)	72.8 (1.30)	1, 12, 35)	
$[Co(OH_2)_6]^{3+}$	49 (1.6)	75 (1.7)	Topp (1928)48)	
$[Co(S_2COC_2H_5)_3]$	48.5 (2.43)	62.5 (2.56)	Kida (1955)52)	
$[Co(S_2CNH_2)_3]$	47.2 (2.45)	62.0 (2.80)	Kida (1955)52)	
$[Co\ carb_3]^{3-}$	46.5 (2.19)	68.2 (2.22)	Mori (1954)47)	

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33) B. Adell, *Acta Chem. Scand.*, **5**, 941 (1951).

34) M.L. Ernsberger and W.R. Brode, *J. Am. Chem. Soc.*, **56**, 1842 (1934).

35) Y. Shimura, H. Ito and R. Tsuchida, *J. Chem. Soc. Japan*, **75**, 560 (1954).

36) H. Kuroya and R. Tsuchida, *J. Chem. Soc. Japan*, **61**. 597 (1940).

37) G. Wilkinson, *J. Am. Chem. Soc.*, **74**, 6148 (1952).

38) A. Nakahara, This Bulletin, **27**, 260 (1954).

39) K. Yamasaki, This Bulletin, **15**, 130 (1940).

40) K. Yamasaki, T. Hara and M. Yasuda, *Proc. Japan Acad.*, **29**, 337 (1953).

41) J.-P. Mathieu, *Bull. soc.chim.* [5] **3**, 463 (1936).

42) J. Brigando, *Compt. rend.*, **236**, 708 (1953).

43) R. Tsuchida and S. Kashimoto, This Bulletin, **11**, 785 (1936).

44) K. Sone, I. Miyake, H. Kuroya and K. Yamasaki, *J. Chem. Soc. Japan*, **69**, 70 (1948).

45) I. Lifschitz, *Rec. trav. chim.*, **69**, 1495 (1950).

46) S. Kashimoto and M. Kobayashi, This Bulletin, **12**, 350 (1937).

47) M. Mori and M. Shibata, *J. Chem. Soc. Japan*, **75**, 1044 (1954).

48) J. Topp, Dissertation, Münster (1928): quoted in "Handbuch der Physik" XXI, p. 59 (1929).

49) K. Nakamoto, M. Kobayashi and R. Tsuchida, *J. Chem. Phys.*, **22**, 957 (1954).

50) F. Basolo, *J. Am. Chem. Soc.*, **75**, 227 (1953).

51) M. Martinette and J.C. Bailar, Jr., *J. Am. Chem. Soc.*, **74**, 1054 (1952).

52) S. Kida and H. Yoneda, *J. Chem. Soc. Japan*, **76**, 1059 (1955).

53) R.G. Yalman and T. Kuwana, *J. Phys. Chem.*, **59**. 298 (1955).

ii) Chelate and polydentate ligands are abbreviated as follows: acac, acetylacetonate ion; carb, chelate carbonate ion; dg, univalent ion of dimethylglyoxime; dien, diethylenetriamine; dip, 2, 2′-dipyridyl; edta, ethylenediaminetetraacetate ion (quadrivalent); en, ethylenediamine; gly, glycinate ion; ox, chelate oxalate ion; phen, 1, 10-phenanthroline; pn, propylenediamine.

iii) Frequency values are given by the unit of 10^{13}/sec.

iv) The bands hidden under the specific absorption bands of the ligands are indicated as (( )).

v) The data asterisked were roughly estimated from the figures of absorption curves in literature.

vi) The references collected under the column, "Supplementary Refs.", are not exhaustive or complete but may provide some information for the details.

Conclusion

From the Tables I–VI, the following series are obtained for the simple ligands:

$$\mathrm{NO_2^-} \quad \mathrm{SO_3^=} \quad \mathrm{en} \quad \mathrm{NH_3} \quad (\mathrm{ONO^-},\ \mathrm{NCS^-},\ \mathrm{OH_2}) \quad \mathrm{ox} \quad (\mathrm{ONO_2^-},\ \mathrm{OSO_3^=}) \quad (\mathrm{OCHO^-},\ \mathrm{OH^-},\ \mathrm{carb},\ \mathrm{OCOR^-}) \quad (\mathrm{OCOCO_2^=},\ \mathrm{OCO_2^=}) \quad \mathrm{SSO_3^=} \quad \mathrm{F^-} \quad \mathrm{N_3^-} \quad \mathrm{Cl^-} \quad \mathrm{OCrO_3^=} \quad \mathrm{Br^-} \quad \mathrm{I^-} \qquad (1)$$

where the ligands in parentheses stand in almost the same positions. For more complicated ligands, the following series are obtained:

$$\mathrm{CN^-} \quad \mathrm{C_5H_5^-} \quad \mathrm{dg} \quad (\mathrm{dip},\ \mathrm{phen}) \quad (\mathrm{dien},\ \mathrm{pn},\ \mathrm{en}) \quad \mathrm{NH_3} \quad \mathrm{gly} \quad \mathrm{edta} \quad \mathrm{acac} \quad \mathrm{ox} \quad \text{polymolybdate-ion} \quad \mathrm{S_2COC_2H_5} \quad \mathrm{S_2CNH_2} \quad \mathrm{carb}. \qquad (2)$$

Miscellaneous notes

(A) Cyanate Ion.—Two broad absorption bands were reported for $K_3[Co(CN)_6]$ at 97.2 ($\log \varepsilon_{\max} = 2.37$) and at 117.0 ($\log \varepsilon_{\max} = 2.08$). Kiss and Czeglédy[10] assigned the two bands to the first and the second bands, but later Kuroya and Tsuchida[36] to the second and the third bands. More recently, Nakamoto, Kobayashi and Tsuchida[49] interpreted the effects of polar solvents no these two bands assuming that the bands are equally the specific bands due to the coordinated cyanate radicals. In view of the above condition, $[Co(CN)_6]^{3-}$ was marked by a question mark in Table VI. But it is very likely that the cyanate ion has an extraordinary high position on the spectrochemical series.

(B) Carbonate and Oxalate Ions.—The unidentate carbonate ion has a lower position on the spectrochemical series than the chelate carbonate ion. This is also true for oxalate radical. In accordance with this fact, carbonato- or oxalato- pentammine Co(III) salts are more unstable than the corresponding tetrammine salts.

(C) Methylamine.—Brigando[42] reported the following data:

	First band	Second band
$[Co(NH_3)_4(NH_2CH_3)_2]Cl_3$	61.9	86.7
$[Co(NH_3)_6]Cl_3$	62.5	88.2

The data show that methylamine stands immediately behind NH_3.

(D) Substituted Ethylenediamines.—Basolo[50] measured the absorption spectra of *trans*-dichlorobis(N- or C-alkylethylenediamine)-cobalt(III) chlorides. From the curves reported by him, it is shown that the first bands of these complexes are displaced towards the longer wave-lengths in the order of

$$\text{en} \quad \text{(C-dimethyl)-en} \quad \text{(C, C}'\text{-tetramethyl)-en} \quad \text{(N-methyl)-en} \quad \text{(N-ethyl)-en} \quad \text{(N-}n\text{-propyl)-en.} \qquad (3)$$

The absorption data reported for some of the propylenediamine complexes[41,25,51] show that propylenediamine has almost the same position in relation to ethylenediamine.

(E) Pyridin.—Few data published for absorption spectra of Co(III) pyridin complexes. But judging from the data on $[Co\ py_4\ NH_3\ Cl]\ Cl_2$[14], it is certain that pyridin comes behind NH_3.

(F) Organic Acids.—Linhard[4] reported that many organic mono-acid-radicals have almost the same positions on the spectrochemical series, but that in the case of mono-, di- or tri-chloro acetic acid some blue shifts occurred in the first and second bands of the acido-pentammine or *cis*-diacido-tetrammine complexes. From the order of the blue shifts, the spectrochemical series of $OCOR^-$ is determined as follows:

$$\mathrm{OCOR^-}:\ \mathrm{R} = \mathrm{CCl_3},\quad \mathrm{CHCl_2},\quad \mathrm{CH_2Cl},\quad \mathrm{CH_3}\ \text{and others.} \qquad (4)$$

Summary

The visible and ultra-violet absorption spectra of many cobaltic ammine, oxalato, carbonato and amino-acido complexes have been determined in solution.

The spectrochemical series for the ligands of Co(III) complexes has been redetermined.

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