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STABILITY AND STEREOCHEMISTRY OF COBALT(II) COMPLEXES WITH STEREOISOMERIC 1,2-DIAMINO-CYCLOPENTANE TETRAACETIC ACIDS

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Abstract—Racemic 1,2-diaminocyclopentane-N,N,N′,N′-tetraacetic acid (CPDTA) has been resolved, by the fractional crystallization of the brucine salt, into its enantiomers giving proof of its *trans*-configuration. Cobalt(II) complexes of (+)-, (−)- and (±)-CPDTA have been prepared in solution and their stability constants measured potentiometrically using a mercury pool electrode. ORD and CD spectra of cobalt complexes containing either (+)- or (−)-CPDTA have been recorded together with u.v. and visible absorption spectra. On the grounds of ORD and visible absorption spectra it is suggested that the complexes exhibit Jahn-Teller splitting.

INTRODUCTION

1,2-DIAMINOCYCLOPENTANE-N,N,N′,N′-tetraacetic acid (CPDTA, was first synthesized by Belcher *et al.*[1] and Yashunskii and Shchukina[2]. Data are available on its pK values and the stability of its alkaline earth complexes [2–4].

EXPERIMENTAL

Stability constants

Stability constants of Hg(II) and Co(II) complexes with CPDTA were determined by a modified pHg method described previously [5]. Using this method, stability constants of both protonated (MHL) and "normal" complexes (ML) can be determined simultaneously. The e.m.f. of the galvanic cell

$$\frac{\mathrm{Hg}(l)}{\mathrm{Gl}}\left|\begin{array}{c}\text{Investigated}\\ \text{solution}\end{array}\right\|\underset{E_{j1}}{}\begin{array}{c}0\cdot1\,\mathrm{M}\\ \mathrm{NaNO_3}\end{array}\left\|\underset{E_{j2}}{}\begin{array}{c}\mathrm{KCl},\\ \text{satd.}\end{array}\right|\mathrm{Hg_2Cl_2}(s),\ \mathrm{Hg}(l)$$

was measured using a Radiometer Titrator TTT 1c in connection with a Scale Expander pHA 630 so that a readout discrimination of ±0·1 mV could be achieved. This potentiometric equipment was

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1. R. Belcher, R. Hoyle and T. S. West, *J. chem. Soc.* 667 (1961).
2. V. G. Yashunskii and M. N. Shchukina, *Khim. Nauka i Prom.* **2**, 662 (1957); *idem. Zh. obshch. Khim.* **28**, 230 (1958).
3. H. Kroll and M. Gordon, *Ann. N.Y. Acad. Sci.* **88**, 34 (1960); *ibid. Federation Proc.* **20**, No. 10, 51 (1961).
4. O. A. Weber, N. Paulić and Lj. Purec, *Arh. hig. rada*, **19**, 55 (1968); see also Vl. Simeon, *ibid.* **19**, (Suppl. No. 1), 99 (1968).
5. Vl. Simeon, B. Švigir and K. Voloder, *Mh. Chem.* **100**, 1854 (1969).

standardized against a Pye Weston Standard Cell. The pH of the equilibrated solutions was measured with the same equipment which was, for this purpose, standardized using solutions of $HClO_4$ (0·1M in $NaNO_3$). Thus, pH is defined in terms of hydrogen-ion concentration rather than activity, as are the constants determined in this work.

The solutions to be investigated were contained in a stoppered glass test-tube having a platinum wire contact through the base. Glass (Radiometer G 202 B) and satd. calomel (K 401) electrodes were introduced from above while a mercury pool served as the mercury electrode.

For determining the stability constants of $Hg(CPDTA)^{2-}$ the potential of mercury and glass electrodes was measured in 10 solutions containing $8{\cdot}6\times10^{-4}$M $Hg(NO_3)_2$ and 1×10^{-3}M (±)-CPDTA whose pH was varied between 2·5 and 4·5. In the investigation of Co(II) complexes the solutions were $1{\cdot}112\times10^{-2}$M in $Co(NO_3)_2$ and $2{\cdot}010\times10^{-4}$M $Hg(NO_3)_2$, 1×10^{-3}M in either (+)-, (−)-, or (±)-CPDTA and pH was varied, by adding adequate amounts of NaOH or HNO_3, between 3 and 5. All these solutions were also 0·1M in $NaNO_3$. Cobalt(II) and mercury(II) stock solutions were previously standardized complexometrically and those of CPDTA by potentiometric titration. The temperature was held at 20·0 ± 0·02°C.

The systems studied are rather inert so that the equilibrium potential and pH were achieved only after 24–48 hr. The criterion for equilibrium was the constancy of both mercury electrode potential and pH.

All the constants were calculated by linear regression analysis of the equations quoted in Ref. [5] so that their standard errors could also be estimated. Acid dissociation constants of CPDTA, taken from Ref. [4], were: $pK_1 = 1{\cdot}87$, $pK_2 = 2{\cdot}44$, $pK_3 = 7{\cdot}48$, $pK_4 = 10{\cdot}09$.

Absorption and ORD spectra

U.V. and visible absorption spectra were recorded using a Perkin Elmer Model 137 U.V. spectrophotometer and ORD spectra using a Cary Model 60 recording spectropolarimeter. The solution contained equimolar amounts of $Co(NO_3)_2$ and CPDTA (0·01M or 0·0001M) or CPDTA alone. CD spectra were recorded using a Cary recording spectropolarimeter fitted with a CD attachment.

Materials

Chemicals were of analytical reagent grade and were not further purified. Water was first de-ionized and then distilled in an all-glass (Pyrex) still.

Cyclopentanediamine(1,2)-dihydrochloride

This was prepared by a modification of the procedure of Jaeger and Blumendal[6] using Al–Ni alloy instead of sodium ethoxide as a reducing agent.

To a stirred solution of 12·8g (0·1 mole) of 1,2-cyclopentanedione–dioxime in 300 ml of water containing 36g of sodium hydroxide 24g of Al–Ni alloy was added over a period of 30 min at 48–50°. The reaction mixture was stirred for an additional 3 hr at this temperature, the alloy removed by suction filtration and the filtrate distilled at normal pressure. The fraction boiling at 107° was acidified with 10 per cent hydrochloric acid to pH 3·5 and the solvent evaporated *in vacuo*. The resulting brown-yellow crystals were purified by refluxing in absolute ethanol, filtered by suction and recrystallized from ethanol, m.p. 300°C (dec.), yield 50 per cent. *Anal.* Calcd. for $C_5H_{14}N_2Cl_2$ (173·10): C, 34·69; H, 8·15; N, 16·19; Cl, 40·97. Found: C, 34·35; H, 8·37; N, 16·19; Cl, 41·18.

1,2-Diaminocyclopentane-N,N,N′,N′-tetraacetic acid was prepared by slightly modified procedure described by Belcher[1]. *Anal.* Calcd. for $C_{13}H_{20}N_2O_8$ (332·31): C, 46·98; H, 6·07; N, 8·43. Found: C, 46·90; H, 5·96; N, 8·53.

The i.r. spectra contained the expected vibrations. Potentiometric titration; tetrabasic acid, purity 98–99 per cent; m.p. 253–255°C.

Preparation of diastereomeric salts

A mixture of 3·322g (0·01 mole) of (±)-CPDTA and 8·60g (0·02 mole) of brucine was dissolved in 200 ml water and about 1600 ml of acetone (p.a.) was added. After standing overnight, 6·5–8·0g (54–67 per cent) of white crystals separated. The less soluble fraction was purified by repeated crystallization from water and acetone until a constant specific rotation $[\alpha]_D - 10°$ (c, 2 per cent in water)

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6. F. M. Jaeger and H. B. Blumendal, *Z, anorg. allg. Chem.* **175**, 161 (1928).

was achieved, yield 80 per cent. The other diastereomer was isolated from the mother liquor by evaporation of the solvent *in vacuo*. A brown–yellow crystalline product (2·5–4·0g; 21–23 per cent) was obtained. The purification of this fraction was carried out in the same way as described above until, after 5 crystallizations, a constant value of $[\alpha]_D - 20°$ (c, 2 per cent in water) was obtained; yield 60 per cent.

Hydrolysis of diastereomeric salts into optically active acids.

A sample (0·3g) of diastereomeric salt was dissolved in 3·0 ml of cold water and after filtration (Schleicher–Schüll, Blue band) the filtrate was acidified with 0·2 ml of 10 per cent hydrochloric acid to pH 2. Crystallization was induced by scratching; yield 0·03g (40 per cent). The last traces of brucine hydrochloride were removed by washing with water to a negative reaction with nitric acid. From the diastereomeric salt with $[\alpha]_D - 10°$ the corresponding acid with $[\alpha]_D + 58°$ (c, 1 per cent in 0·1N NaOH) was obtained, while the brucine salt with $[\alpha]_D - 20°$ gave (–)-CPDTA with $[\alpha]_D - 53°$ (c, 1 per cent in 0·1N NaOH). A sample was dried for analysis at 80–100°C.

RESULTS

Typical reproducibility of pH and e.m.f. measurements was about ±0·02 pH and ±0·8 mV, respectively, provided that equilibrium had been achieved. The constants determined are quoted in Table 1. These are defined by following expressions:

$$\beta_{111} = \frac{[MHL]}{[M][H][L]}, \beta_{101} = \frac{[ML]}{[M][L]}$$

where L denotes the tetranegative CPDTA anion, M the metal cation and H the proton. Ionic charges are omitted, here and elsewhere, in the sake of clarity.

Table 1. Stability constants of Co^{II} and Hg^{II} complexes with *trans*-1,2-CPDTA (± standard errors)

Metal	No. of detns.	Stereoisomer	$\log \beta_{101}$	$\log \beta_{111}$
Hg^{II}	10	(±)	23·24 ± 0·13	26·01 ± 0·08
Co^{II}	9	(±)	12·00 ± 0·04	15·41 ± 0·02
	5	(+), (–)	12·14 ± 0·06	15·47 ± 0·04

ORD spectra of the (+)-CPDTA alone and of the mixtures Co + (+)-CPDTA and Co + (–)-CPDTA are shown in Fig. 1. CD spectra of Co^{II}-(+)-CPDTA and Co^{II} + (–)-CPDTA are reproduced in Fig. 2. Visible and u.v. spectra of CPDTA, Co(CPDTA) and $Co(NO_3)_2$ are shown in Fig. 3.

DISCUSSION

Ligand configuration

Since it was possible to resolve CPDTA into enantiomeric forms it is evident that the synthesis described led to the *trans*-isomer. Although some *cis*-isomer may have been present in the product the presence of an appreciable amount is unlikely since this should affect the values of the stability constant of the Co(±)-CPDTA complex relative to analogous complexes containing either (+)- or (–)-

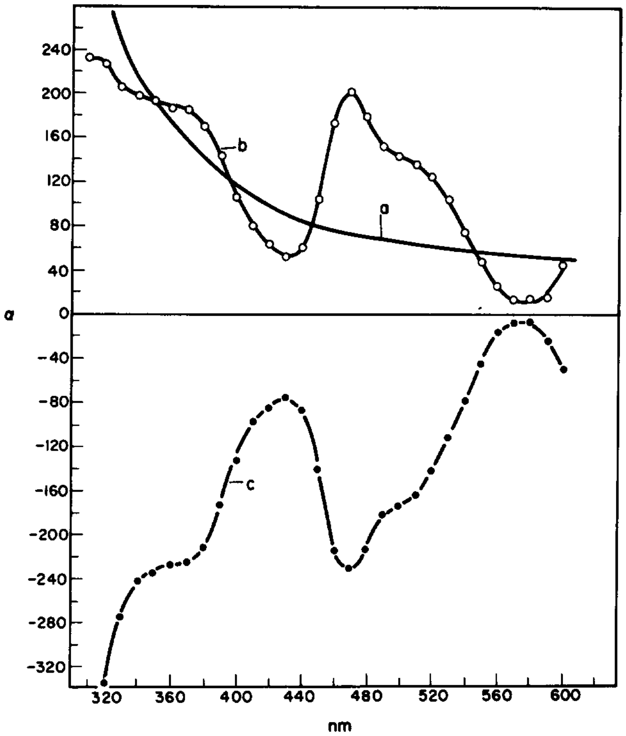

Fig. 1. Rotatory dispersion spectra of (+)-CPDTA (*a*), Co-(+)-CPDTA (*b*), and Co-(−)-CPDTA (*c*).

CPDTA (see the results of Basolo *et al.*[7] with the complexes of *meso*- and (±)-isomers of 2,3-diaminobutane and stilbenediamine).

Dunlop, Gillard and Wilkinson [8] have established the absolute configurations of several diamines. The ORD spectrum of (+)-CPDTA indicates that this compound can be related to (+)-propylenediamine (pn) and (+)-cyclopentanediamine (cptn) which also exhibit plain positive ORD curves. Analogously, (+)-PDTA (propylenediamine–tetraacetic acid) is related to (+)-pn [9]. The absolute configuration of (+)-CPDTA can therefore be denoted as (S)-*trans*, i.e. as being related to (S)-(+)-alanine.

Co^{II}-*CPDTA complexes*

There are four possible isomeric complexes in the system containing cobalt(II) and enantiomeric forms of CPDTA. Their configurations can be denoted as *kl*, *k'l*, *kl'* and *k'l'*, according to the following formulae (*k* and *l* refer to central atom and ligand configurations, respectively):

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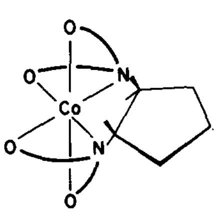
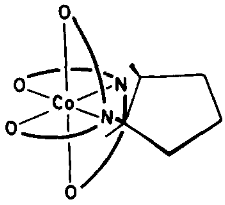
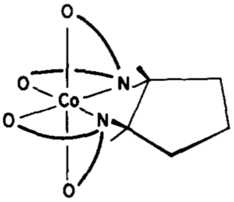
7. F. Basolo, Y. T. Chen and R. K. Murmann, *J. Am. chem. Soc.* **76**, 956 (1954).
8. H. J. Dunlop, R. D. Gillard and G. Wilkinson, *J. chem. Soc.* 3160 (1964).
9. F. P. Dwyer and F. L. Garvan, *J. Am. chem. Soc.* **83**, 2610 (1961).



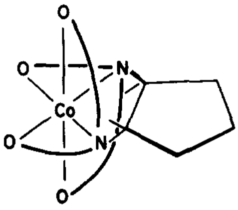
kl



k'l'



kl'



k'l

Configurations *kl and k'l'* are related as antipodes as are *k'l* and *kl'*. From ORD and CD spectra (see Figs. 1 and 2) it is evident that the complexes Co(+)CPDTA and Co(−)CPDTA are antipodes since respective spectra are clearly related as mirror images with respect to the zero line. Using scaled atomic models (Griffin & George Courtauld's models) it is found that only *kl* and *k'l'* configurations are possible. This is in agreement with the ORD and CD spectra. The central atom configuration *k* is identical to the absolute configuration *L* as defined for Co^{III}–EDTA complexes[10]. Accordingly it can be concluded that the absolute configuration of the dextrorotatory complex is *L*-[Co(*S*-(+)-CPDTA)] (corresponding to our *kl* configuration), while the laevorotatory complex is its antipode, *D*-[Co(*R*-(−)-CPDTA)] (or *k'l'*). The designations *L* and *D* for central atom configuration were adopted for the sake of consistency with other work, while the ligand configuration is denoted as either *S* or *R* (referring to C_1 and C_2 atoms) as defined in the previous paragraph. Unfortunately, these conclusions cannot be substantiated by additional ORD and/or CD data on related Co^{II} complexes since, as far as we are aware, such spectral data are lacking.

In contrast to the spectra observed with similar Co^{III} complexes the rotatory dispersion spectra of Co^{II}–CPDTA chelates are rather complicated. The ORD spectrum shows at least six inflexion points (λ: 320, 400, 450, 480, 540, > 600 nm) while in the *CD* spectrum there are six maxima (λ_{max}: 300, 360, 395, 450, 535, > 600 nm) which roughly coincide with these (except for those at 360 and 480 nm). According to this, there are at least five Cotton effects in the region 300–600 nm.

Stability constants of Co^{II}CPDTA and Co^{II}H(CPDTA) complexes are not affected by the isomeric form of the ligand, (Table 1). This is in accordance with

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10. T. E. MacDermott and A. M. Sargeson, *Austral. J. Chem.* **16**, 334 (1963).

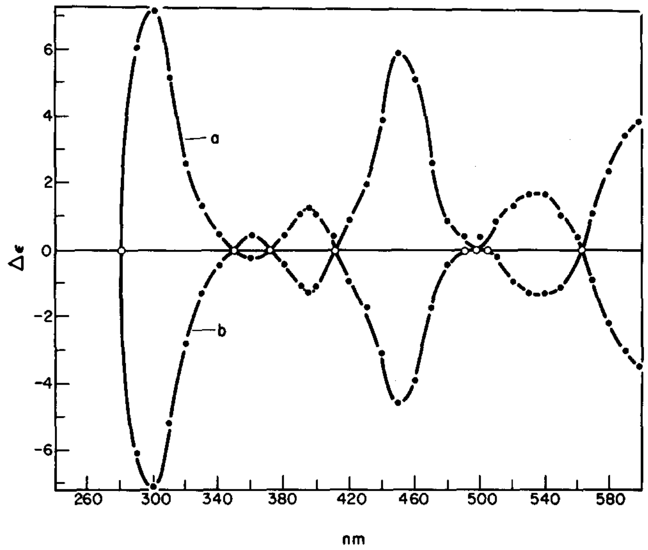

Fig. 2. Circular dichroism of Co-(+)-CPDTA (*a*), and Co-(−)-CPDTA (*b*).

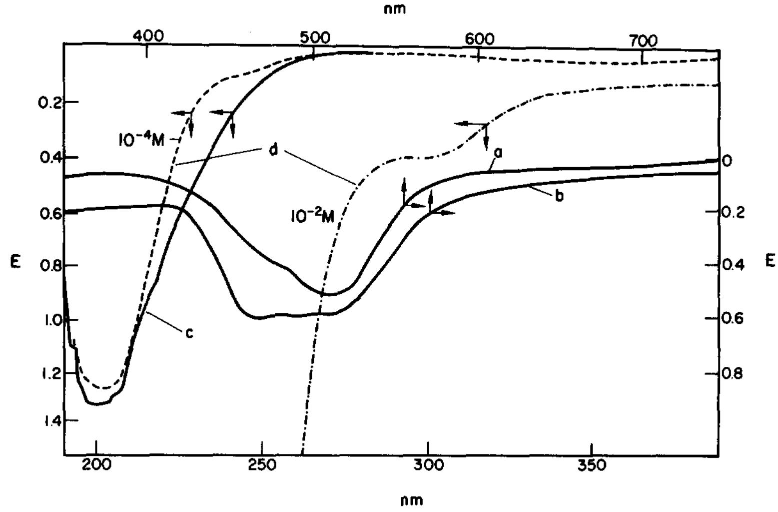

Fig. 3. Visible absorption spectra of $Co(NO_3)_2$ (*a*) and Co-(±)-CPDTA (*b*), and UV spectra of (±)-CPDTA (*c*) and Co-(±)-CPDTA (*d*).

recent data on complexes containing optically active ligands[11–13]. This was tested by using Student's *t*-test.

It is interesting to note that both Hg^{II} and Co^{II} complexes with CPDTA are considerably less stable than the corresponding EDTA complexes[5]. This can

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11. R. D. Gillard, H. M. Irving, R. M. Parkins, N. C. Payne and L. D. Pettit, *J. chem. Soc.* 1159 (1966).
12. VI. Simeon and O. A. Weber, *Croat. Chem. Acta* **38**, 161 (1966).
13. J. H. Ritsma, G. A. Wiegers and F. Jellinek, *Recl. Trav. Chim. Pays-Bas* **84**, 1577 (1965).

only partially be explained by the somewhat lower basicity of CPDTA relative to EDTA (for EDTA $pK_4 = 10{\cdot}26$[14], while for CPDTA $pK_4 = 10{\cdot}09$[4]). On the grounds of the stability data available, a well-founded interpretation for this cannot be given.

From the absorption spectra reproduced in Fig. 3, it can be seen that the cobalt absorption band is considerably broader for the complex (λ_{max} 460–520 nm) than for the cobaltous nitrate solution (λ_{max} 510 nm). In the region 450–540 nm the ORD curve shows three inflexion points and CD spectrum three maxima indicating that some, or all of the metal–ligand bonds, are active chromophores. The shape of both the absorption and the ORD spectra in this region indicate the possible existence of a Jahn–Teller splitting. This is theoretically possible in Co^{II} complexes with ligands whose fields are stronger than that of water.

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14. G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta* **30**, 1798 (1947).