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Copper(II) and Cobalt(II) Complexes with L-Threonine and L-*allo*-Threonine: Potentiometric and CD-Spectroscopic Study

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Stability constants of cobalt(II) and copper(II) complexes with L-threonine and L-*allo*-threonine as well as ligands' acid dissociation constants were determined by potentiometry. Circular-dichroism spectra of the investigated complex solutions were recorded in a broad pH range and resolved into the contributions of individual dichroic species applying a recently developed regression procedure with iterative weighting. Two new deprotonated cobalt(II) complexes, $[Co(Thr)_2H_{-1}]^-$ and $[Co(aThr)_2H_{-1}]^-$, were detected and characterized by stability constants and CD spectra. New CD bands were found in the UV region for the complexes of both metals. Tentative structure types for the deprotonated as well as for their parent complexes were inferred from the stability data.

INTRODUCTION

Despite their common use in various branches of coordination chemistry the spectroscopic methods for studying complex compounds in solution have not been developed enough to match the degree of perfection of the instrumentation currently available. Comparatively recently some powerful methods of linear algebra and linear statistics have been successfully applied to a variety of analytical problems.[1,2,3] It is evident that some of these could be advantageously used in the studies of coordination equilibria in solution. One of typical problems in this field is the determination of the spectra of individual complex species standing in a labile equilibrium. In the present paper a method of multilinear weighted regression described recently[4] is applied for the estimation of circular-dichroism spectra of cobalt(II) and copper(II) complexes with diastereomeric threonines (L-threonine = Thr, and L-*allo*-threonine = aThr). The necessary stability constants were redetermined by potentiometry employing a modified version of the pH calibration method originally developed by Irving and co-workers.[5] The data were collected for broader wavelength and pH ranges than was the case in earlier works.[6,7,8] Whenever spectra contained overlapping bands a combined linear/nonlinear method of decomposition into Gaussian component bands was used.

MATERIALS AND METHODS

The chemicals were of the analytical reagent grade (or equivalent) and were not further purified. Water was first deionized and then distilled in an all-glass still in the presence of a minute amount of $KMnO_4$.

Potentiometry

Ligand solutions contained L-threonine or L-*allo*-threonine (3 mmol L^{-1}), HNO_3 (*ca.* mmol L^{-1}) and $NaNO_3$ (0.1 mol L^{-1}). Stock solutions of $Co(NO_3)_2$ and $Cu(NO_3)_2$, containing also $NaNO_3$ (0.1 mol L^{-1}), were standardized complexometrically.

The titrations were carried out under nitrogen gas (prepurified to remove O_2 and CO_2) in a 25 mL glass vessel thermostated to (25 ± 0.05) °C. A carbonate-free NaOH solution (0.1 mol L^{-1} with the same $NaNO_3$ background) served as the titrant; it was standardized against potassium hydrogen phthalate. In the experiments for p*K* determination one of the above ligand solutions was titrated; for the determination of the stability constants the solution to be titrated contained an adequate amount of Co^{2+} or Cu^{2+} ($C_M \leq C_L/2$). The initial volume of the titrate was 15 mL, the maximum titrant addition 3 mL (the individual portions varying between 0.2 and 0.02 mL), and the burette readability 2 μL. The equilibrium e.m.f.'s of the cell, consisting of Radiometer glass (G 202 B) and calomel (K 401) electrodes, were measured to the nearest 0.1 mV by means of a Radiometer pHM 64 digital voltmeter; this instrument was calibrated against a certified Weston cell.

The apparatus was standardized on the conventional pH scale[9] by measuring the e.m.f. in five buffer solutions (S: HCl/KCl, KH phthalate, equimolal phosphate, borax and $Ca(OH)_2$). This pH calibration was consistent within ± 0.009 and was found to be superior to the usual two-point calibration for which the r.m.s. deviation about the regression line *E* vs. pH(S) was typically ± 0.02 with the same electrodes.

In subsequent computations pH had to be converted into the »stoicheiometric« value, ph:

$$\mathrm{ph} = \lg\{[\mathrm{H}^+]/(\mathrm{mol\ L^{-1}})\}; \qquad (1)$$

the two values, according to Irving *et al.*[5], differ by an approximately constant amount:

$$\mathrm{ph} = \mathrm{pH} + A. \qquad (2)$$

The initial value, A^0, was first determined, as originally recommended, from the titration of a strong acid (actually HNO_3) and was then refined during the computations of ligand p*K* values.[5] The refinement consisted of repetitive MINIQUAD 75[10] (»hybrid«) runs in which the assumed *A* values were systematically varied. The optimum value, $\hat{A}$, i. e. that which gave the minimum variance about the observed titration curve, was then used to convert pH into ph in subsequent MINIQUAD computations of the cumulative stability constants of metal complexes. These are here defined, for a generalized species ($M_qL_nH_p$), as follows:

$$\beta_{qnp} = [\mathrm{M}_q\mathrm{L}_n\mathrm{H}_p]/[\mathrm{M}]^q\,[\mathrm{L}]^n\,\mathrm{h}^p = \beta^{\ominus}_{qnp}\,(c^{\ominus})^{1-q-n-p} \qquad (3)$$

where $c^{\ominus}$ = mol L^{-1} (the choice of the standard states was discussed elsewhere[11]).

Circular-dichroism spectra

The solutions prepared for CD work had a similar composition to those employed in potentiometric experiments, the only difference being the omission of $NaNO_3$. The C_L/C_M ratio was kept near 2 and the proportions of individual species were varied by varying pH of the solutions in the range $2 < \mathrm{pH} < 11$. The spectra were recorded with a JASCO J-20 spectropolarimeter (calibrated with L-camphor-10-sulphonic acid) in the (250 ... 650) nm range.

In order to resolve the solution spectra into the contributions of individual dichroic species it was necessary to know the species distribution in each of the solutions. This was calculated from the analytical concentrations (C_M and C_L), measured pH values (which were, of course, converted into ph's) and the stability constants which were determined independently. Perrin's COMICS procedure[12] was applied for this purpose. The result of this computation were concentrations, c_{ij}, of *J* present species in *i*-th solution; these were then recalculated into fractional concentrations, a_{ij}, by dividing each c_j by total metal concentration, $C_{M,i}$ (only metal complexes showed dichroism in the examined wavelength range).

The ellipticities measured in i-th solution ($i = 1, \ldots, I$) at k-th wavelength ($k = 1, \ldots, K$) were normalized by being divided by the length of optical path and total metal concentration:

$$\Theta_{ik} = \Theta_{ik}/lC_{\mathrm{M},i}. \tag{4}$$

The overall spectral signal, Θ_{ik}, is the sum of the signals of individual dichroic species. Assuming a linear relation between ellipticity and concentration, one may write

$$\Theta_{ik} = \sum_{j} a_{ij}\,\psi_{jk} \tag{5}$$

where ψ_{jk} is the ellipticity of j-th species at k-th wavelength. Eq. (4) may be more concisely rewritten in the matrix from:

$$[\Theta_{ik}] = [a_{ij}]\,[\psi_{jk}] \tag{6}$$

or

$$\Theta = \mathrm{A}\,\psi \tag{6a}$$

Now, the problem of computing the spectra of individual species is clearly the one of least-squares solution of linear system (6) to find the optimized set of species spectra, ψ. A possible way of solving Eq. (6) is a multiple linear regression. The iterative regression algorithm applied here was described earlier[4]. It is applicable in those cases when the variances of spectral measurements or, at least, the qualitative relation of the weighting function and the expectance of the measured values are known.

When the spectrum of a complex species contained overlapping peaks (or the peaks were pronouncedly asymmetric) the peak positions were estimated by means of a non-linear decomposition procedure, assuming a Gaussian shape of the bands. The procedure is based upon a *quasi*-Newtonian method of minimum search[13], the object function being the sum of squared residuals. In order to reduce the number of parameters which are to be guessed before the computation the linear (intensity) parameters were separated in the first regression cycle, as was suggested by Lawton and Sylvestre[14], i. e. they were computed by a linear regression using the guessed values for the non-linear parameters (positions and half-widths of the peaks). This separation was not used in subsequent refinement cycles in which all parameters were refined by means of the mentioned non-linear regression routine.

The decomposition procedure failed to converge in some cases so that the peak positions had to be estimated directly from the spectrum. In these cases only the maxima and minima were recognized as peaks while the shoulders were disregarded because the position of a shoulder may be considerably different from that of the respective peak.

RESULTS

The results of potentiometric measurements are summarized in Tables I (pK values)and II (lg $\beta^{\ominus}_{qnp}$ values). Standard errors of the constants, as output by MINIQUAD, are given in the parentheses (in units of the last decimal place). The internal consistency of the data, as can be seen from these values, can be judged as satisfactory. Their accuracy, however, is definitely lower. This can be clearly seen by comparing the standard errors in Table II with the uncer-

TABLE I

Acid Dissociation Constants of Threonine Epimers, $T = 298.2$ K, $[\mathrm{NaNO_3}] = 0.1$ mol/L, $C_\mathrm{L} = 3$ mmol/L

Ligand	pK_1	pK_2
L-Thr	2.20(1)	8.89(1)
L-*allo*-Thr	2.11(9)	8.83(3)

TABLE II

Stability Constants of Copper(II) and Cobalt(II) Complexes with Threonine Epimers; T = 298.2 K, $[NaNO_3]$ = 0.1 mol/L, C_L = 3 mmol/L, $C_L/C_M \approx 2$.

Ligand	Metal	$\lg \beta^{\ominus}_{110}$	$\lg \beta^{\ominus}_{120}$	$\lg \beta^{\ominus}_{12-1}$	$\lg \beta^{\ominus}_{12-2}$
L-Thr	Cu^{+2}	7.893(6)	14.538(8)	4.79(1)	—5.78(1)
	Co^{+2}	4.298(5)	7.762(6)	—1.94(1)	—
L-*allo*-Thr	Cu^{+2}	7.591(7)	14.005(9)	4.33(1)	—6.22(1)
	Co^{+2}	4.13(2)	7.17(4)	—2.28(3)	—
D-Val*	Cu^{+2}	7.88	14.52	—	—
α-AABA**	Cu^{+2}	8.32(1)	15.45(1)	—	—
	Co^{+2}	4.16(4)	7.85(2)	—	—

* Vl. Simeon and V. Cafuk, unpublished data (1968): T = 293.2 K, $[NaNO_3]$ = 0.37 mol/L.

** AABA = α-aminobutyrate (Šoštarić and Simeon[20]; measured at 298.2 K, $[NaNO_3]$ = 0.1 mol/L).

tainty of the pH calibration (± 0.009): 6 out of 14 standard errors are lower than that which is physically impossible (this could not be noticed had only the common two-point calibration been done). Further, one has to be aware of the uncertainties in the total concentrations of dissociable hydrogen, metal and ligand which are all around 0.2 per cent. In order to estimate the over-all uncertainty in β values the partial derivatives, approximated by $\Delta \lg \beta / \Delta A$, $\Delta \lg \beta / \Delta C_H$, $\Delta \lg \beta / \Delta C_M$ and $\Delta \lg \beta / \Delta C_L$, were calculated using the above guess values for the standard deviations. Assuming, as a first approximation, that the individual error sources are independent, the combined variances in $\lg \beta$ were then easily computed. These are typically near 0.036, corresponding to a standard deviation of ± 0.19 which is a surprisingly high value. Most of the variance is contributed by the uncertainty in pH calibration (60 . . . 95 per cent), the error in C_H being next important factor (5 . . . 25 per cent); errors in C_M and C_L account only for a few per cent of the total variance while the »standard errors« contribute a negligible amount (some 0.2 per cent) to the over-all variability. Had the pH calibration been ten times more accurate (which is the reproducibility of the best glass electrodes currently available) the over-all standard deviation would be around ± 0.05 in the considered case (copper threoninates). This seems to be near the ultimate accuracy attainable when determining the stability constants of metal complexes using volumetric techniques and a glass electrode.

It can be concluded from this error analysis that the results obtained in the present work essentially agree with existing data.[7,8] The differences between these values and those reported by Ivičić and Simeon[8] seem to be manly due to the difference in pH calibration.

The positions and estimated intesities of CD peaks of metal complexes investigated are shown in Table III (Co^{2+} complexes) and Table IV (Cu^{2+} complexes). In all cases, the applied least-squares procedure was successful: the iterative weighting alforithm was convergent and also led to a substantial normalization of the distribution of regression residuals (although in some cases slightly leptokurtic distributions were arrived at). From an analysis of errors it was concluded that the main source of uncertainty were the errors in the **A** matrix (Eq. 6) rather than the errors in measuring the ellipticity.

TABLE III

Positions, λ_m/nm, *and Intensities,* ψ_m/(^{0} dm^2 mol^{-1}), *of the Peaks in CD Spectra of Copper(II) Complexes with* L-*Threoninate* (L) *and* L-allo-*Treoninate* (L′)

$(\mathrm{CuL})^+$	278			
	—204			
$(\mathrm{CuL_2})$	285	610		
	—102	— 92		
$(\mathrm{CuL_2H_{-1}})^-$	295	578	688	
	+433	—136	+ 54	
$(\mathrm{CuL_2H_{-2}})^{-2}$	308	481*	569*	673*
	+222	+ 8	—456	+ 73
$(\mathrm{CuL'})^+$	275			
	— 52			
$(\mathrm{CuL'_2})$	280	620		
	— 16	—169		
$(\mathrm{CuL'_2H_{-1}})^-$	275	≈ 575		
	—322	≈—140		
$(\mathrm{CuL'_2H_{-2}})^{-2}$	280	540		
	—131	—176		

* Data marked with an asterisk were obtained by means of a deconvolution procedure; the remaining values were read off from the graph of the respective component spectrum.

TABLE IV

Positions, λ_m/nm, *and Intensities,* ψ_m/(^{0} dm^2 mol^{-1}), *of the Peaks in CD Spectra of Cobalt(II) Complexes with* L-*Threoninate* (L) *and* L-allo-*Threoninate* (L′)

$(\mathrm{CoL})^+$	239*	271*	295*	403*	536*	552*
	— 78	+ 45	— 45	+ 49	—261	+168
$(\mathrm{CoL_2})$	237*	268*	303*	405*	559*	595*
	+ 49	— 44	+ 72	—105	+104	+113
$\mathrm{CoL_2H_{-1}})$	284*	302*	415*	541*	629*	
	—397	+546	—162	+335	+ 44	
$(\mathrm{CoL'})^+$	≈ 360	440	487	544		
	≈ +100	—212	+ 61	—168		
$(\mathrm{CoL'_2})$	≈ 335	410	558			
	≈— 40	+ 28	+ 53			
$(\mathrm{Col'_2H_{-1}})^-$	≈ 384	440	488	540		
	≈ + 35	— 33	+ 11	— 58		

* Data marked with an asterisk were obtained by means of a deconvolution procedure; the remaining values were read off from the graph of the respective component spectrum.

DISCUSSION

Equilibrium constants

The titrations have revealed the existence of deprotonated cobalt(II) complexes, namely $[\mathrm{Co(Thr)_2H_{-1}}]^-$ and $[\mathrm{Co(aThr)_2H_{-1}}]^-$ which, to the best of authors' knowledge, have not yet been observed. The existence of these species was subsequently confirmed by the analysis of circular-dichroism spectra (see next section).

As is well known[6,7,8,11] the natural diastereomer of threonine forms more stable complexes than the *allo* diasteroeomer does. This was once more confirmed by the stability data measured in the present work. Table II shows that the same applies to the deprotonated complexes as well. The observed stability differences can be explained by conformational energy differences.[15]

Since bis-ligand complexes, ML_2, behave as weak acids releasing one (CoL_2) or two (CuL_2) protons at sufficiently high pH values, it is interesting to compare their pK values which are easily calculated from the cumulative stability constants found in Table II. The pK value of the complex having a composition of $M_qL_nH_p$ is given by

$$\mathrm{p}K\,(qnp) = \mathrm{lg}\,\frac{\beta^{\ominus}{}_{qnp}}{\beta^{\ominus}{}_{qn(p-1)}} \tag{7}$$

These values are displayed in Table V. It can be seen that the pK's of all ML_2 complexes are of a similar magnitude (9.64 ± 0.15), irrespective of the ligand configuration and the kind of the central atom. Next dissociation step is observed only for copper complexes and is weaker by roughly one order of magnitude: p$K\,(12 - 1) = 10.56 \pm 0.01$.

There has been considerable disagreement regarding the structure of threoninato complexes. Various possible structures of ML_2 and ML_2H_{-1} complexes are schematically depicted in Figure 1. Structures I and V were pro-

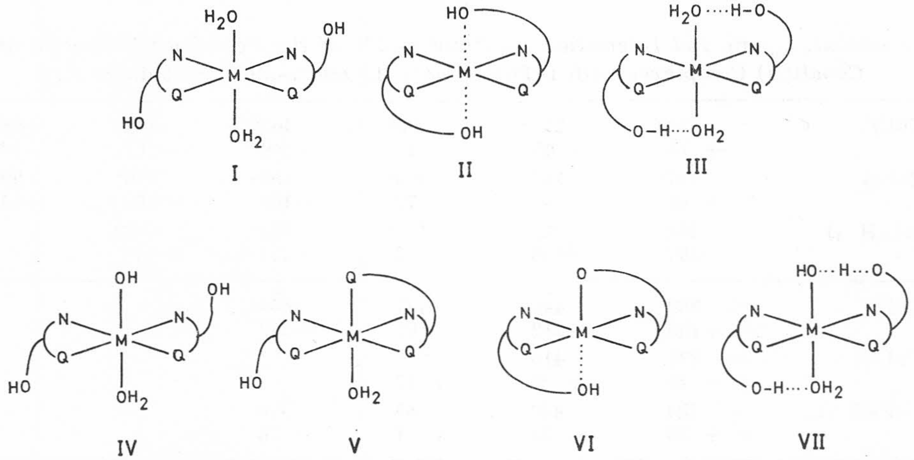

Figure 1. Possible structures of ML_2 and ML_2H_{-1} complexes in aqueous solution (M: Co^{2+}, Cu^{2+}; L: threoninate or *allo*-threoninate anion; Q: acidic carboxylate oxygen).

TABLE V

Acid Dissociation Constants of Cobalt(II) and Copper(II) Complexes with Diastereomeric Threonines

Species	pK
$[Cu(Thr)_2]$	9.75
$[Cu(aThr)_2]$	9.68
$[Co(Thr)_2]$	9.68
$[Co(aThr)_2]$	9.46
$[Cu(Th)_2H_{-1}]^-$	10.57
$[Cu(aThr)_2H_{-1}]^-$	10.55

posed by Grenouillet *et al.*[7] and Rossi *et al.*[16], while Nagypál *et al.*[17] on the ground of NMR data on proton exchange kinetics suggest structures like II and VI. There is another possibility, namely deprotonation of structure I into a hydroxido complex (IV) similar to $[Cu(Ala)_2OH]^-$ complex recently inferred by Gillard and his associates[18] from pH titration data. However, if p*K* values from Table V are compared to the p*K* of Gillard's complex (p*K* (120) = 12.17) this possibility can be safely discarded. According to the results of conformational analysis by Raos and Simeon[15,19] the structures I and V are not very likely. These terdentate structures seem to be hardly reconcilable with the values of stability constants of Cu^{2+} complexes with valine as well as with those for Cu^{2+} and Co^{2+} α-aminobutyrates[20] (these values are included in Table II for the sake of comparison) becauses bidentate, »glycine-like« AABA and valine complexes are more (or equally) stable than the corresponding threoninates. The same reasoning would suggest that structures III and VII could be more likely than II and VI, though it should be admitted that these two sets of structures are so similar in many respects and therefore very difficult to differentiate experimentally. Nevertheless, structures III and VII seem to fit better the experimental findings: the deprotonation process III $\leftrightarrows$ VIII + H^+ does not include closure of an additional ring or a molecular rearrangement, the conformational changes, if any, being very small; the changes in electronic (visible and CD) spectra could be possibly accounted for by the loss of one positive particle and a subsequent charge redistribution.

Circular-dichroism spectra

As was already stated, the applied multiple regression algorithm with iterative weighting[4] proved quite successful. In all cases the final results met all (or nearly all) of the preset criteria (rank of Θ matrix, χ^2, Student's *t*, coefficients of skewness and of excess kurtosis of the residuals' distribution, etc.). Therefore, it seems that the computed spectra of individual complex species are reasonably accurate. Of course, they are subject to various experimental errors, falling into three main classes: (*a*) spectrometric errors (uncertainties in wavelength and ellipticity), (*b*) errors in preparing the solutions for spectroscopic work (analytical and pH-metric errors), (*c*) errors in stability constants. The errors from clas (*a*) influence only the Θ matrix while those from classes (*b*) and (*c*) influence both **A** and Θ matrices. The spectrometric uncertainties or, more precisely, their random component, are taken into account by introducing statistical weights, while (*b*) and (*c*) errors remain outside any linear model. It is well known that any regression procedure gives correct, MVU result (i. e. *m*inimum-*v*ariance *u*nbiased estimates) provided the »independent variables« (**A** matrix) are free from error or, at least, are known with a much higher accuracy than the members of the observational matrix (Θ). Evidently, **A** matrices in the present case do not meet this condition: their members (*i. e.* the concentrations of various species in various solutions) bear both (*b*) and (*c*) errors. Therefore, it must be admitted that the method applied can yield somewhat biased results; this bias, however, is almost certainly small so that basic features of the species spectra are by no means distorted. This can be concluded both from comparison with the data of other authors and from the consideration of possible uncertainties in all values used in computing the **A** matrix.

Copper Complexes. CD spectra of copper(II) threoninates have been investigated by several workers.[7,8,21,22] The peak positions and their signs determined in the present paper (*cf.* Table III) agree with most of the literature data, minor dicrepancies being almost certainly due to the different processing of the raw data. It should be mentioned that the spectral range of the instrument employed here was somewhat narrowed because of its unreliability (noise and/or baseline shift) at both ends of the wavelength scale. Besides well-known ligand-field bands in the visible part of the spectrum an intense band was found near 300 nm in virtually all of the complexes examined. This peak is negative for $[CuThr]^+$ and $[Cu(Thr)_2]$ but it changes its sign upon the deprotonation of the latter complex. Peculiar enough, no such sign inversion is observed for *allo*-threoninato complexes. It seems that this — probably charge-transfer — band has not been reported so far.

Cobalt complexes. The spectra of cobalt threoninates contain more peaks than the corresponding copper complexes. These peaks are not always easy to disclose by any decomposition procedure. Further, it should be pointed out that the individual species exhibit appreciably different CD spectra so that »deconvolution« applied to the spectra of mixtures (method employed by Katzin in his studies of transition metal aminoacidates[23]) may be unreliable. Nevertheless, the spectra of cobalt(II) threoninates agree reasonably well with those recorded by Katzin for Co(II) serinates[23] and agree well with those obtained earlier in our laboratory.[8] Many of the bands in cobalt aminoacidates have been tentatively assigned[23] to certain electronic transitions, using a correlation digram constructed by Liehr[24] who assumed an O_h symmetry around the cobalt(II). No such attempt will be made here because of our rather scarce knowledge of the actual symmetry of the environment of the central atom (is it O_h or D_{2h} or C_2?). An additonal reason for refraining from making any such assignment is some possible bias in the data (*vide supra*). The situation is further complicated by the extremely complex and insufficiently reliable procedure for identifying the peaks. With the presently available decomposition procedures it is very difficult to obtain unambiguous results with strongly overlapping bands, although such procedures are still preferable to the visual peak finding which is permissible only for isolated peaks.

However, the experimental and computational methods applied in this work were sufficiently reliable as to permit an independent proof of the existence of two deprotonated species, $[Co(Thr)_2H_{-1}]^-$ and $[Co(aThr)_2H_{-1}]^-$, which were inferred from potentiometric results. For all of the cobalt threoninates examined there is at least one band in the near UV region which is probably of the ligand-field origin. For the complexes of the natural diastereomer two or three bands were found at $\lambda \leqslant 300$ nm.

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SAŽETAK

Kompleksi bakra(II) i kobalta(II) s L-treoninom i L-*allo*-treoninom: potenciometrijska i spektroskopska (CD) istraživanja

Z. Kralj, N. Paulić, N. Raos i Vl. Simeon

Metodom potenciometrijske titracije određene su konstante stabilnosti kompleksa kobalta(II) i bakra(II) s L-treoninom i L-*allo*-treoninom, kao i konstante kiselinske disocijacije tih liganada. Spektri cirkularnog dikroizma (CD) otopina koje su sadržavale smjesu proučavanja kompleksa (u širokom rasponu pH) resolvirani su u spektre pojedinih kompleksnih vrsta. Otkrivena su dva nova deprotonirana kompleksa, koji su karakterizirani konstantama stabilnosti i spektrima CD kompleksa obaju metala. Predložene su strukture deprotoniranih kompleksa kao i njihovih matičnih kompleksa.