# SCIENTIFIC WORK OF DUŠAN J. RADANOVIĆ: COORDINATION CHEMISTRY OF HEXADENTATE EDTA-TYPE LIGANDS WITH METAL IONS

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ABSTRACT. This article is dedicated to the memory of Dušan J. Radanović, Professor of Inorganic Chemistry at the Faculty of Science, University of Kragujevac, who died in April 2002. The article consists of two parts. In the first part a brief review of Radanovic's scientific work is presented. The second part is the list of all scientific papers published during his life. In this way we want to express our appreciation for his contribution to the development of coordination chemistry in Serbia as well as his contribution to the development of the Faculty of Science in Kragujevac.

#### 1. Review of the scientific work of Dr. Dušan J. Radanović\*

The first research of Dr. Dušan J. Radanović was concerned with synthesis and characterization of cobalt(III) complexes with different amino acids. The reactions of hexanitrocobaltate(III) with different amino acids (glycine, DL-alanine, D-alanine, L-alanine,  $\beta$ -alanine, L-aminobutyric acid, aminoisobutiric acid, L-norvaline, L-leucine, L-norleucine, and L-isoleucine) have been investigated. In these reactions different dinitrobis(aminoacids)cobaltate(III) complexes have been obtained and characterized.

<sup>&</sup>lt;sup>\*</sup> Dušan J. Radanović was born in Kotor Varoš (Bosnia and Herzegovina) in 1933 where he attended primary and secondary school (1948-1953). He studied chemistry at the Faculty of Science, University of Belgrade (1953-1962), where he received his M.S. degree (1968) and Ph.D. (1971) in inorganic chemistry. His first employment was as Assistant at the Faculty of Science in Belgrade (1963-1974). After spending two years (1972-1974) as a Research Fellow at the University of Pittsburgh in USA he was appointed as Assistant Professor (1974), Associate Professor (1982), and Full Professor (1985) at the Faculty of Science, University of Kragujevac. After retirement in 1998 Dr. Radanović was also very active. He used to come to the Department every day until he died in April 2002. His research interests were concerned with structural coordination chemistry and he published about 71 papers.

For characterization of cobalt(III) complexes with aminoacids electronic absorption, infrared and <sup>1</sup>H NMR spectra have been applied. Most of these complexes were resolved into optical isomers and their circular dichroism spectra have been studied [1-9].

During the postdoc stay at the University of Pittsburgh Dr. Radnović began to study optical activity and stereochemistry of the transition metal complexes with aminopolycarboxylate edta-type (edta is ethylenediaminetetraacetate) and related ligands. His interest in this field was mainly focused on the two directions: i) synthesis and characterization of cobalt(III), chromium(III) and rhodium(III) complexes with edta-type ligands, and ii) determination of the influences of various structural changes of the ligand and geometry of the corresponding complexes on the optical activity of octahedral transition metal complexes.

Ethylenediamine-*N*,*N*'-diacetate-*N*,*N*'-di-3-propionate ligand (eddadp) has been used for synthesis of hexadentate Co(III), Cr(III) and Rh(III) complexes. This ligand in relation to the edta has two longer carboxylate chains and in reaction with metal(III) ions three geometrical isomers ( $trans(O_5)$ ,  $trans(O_5O_6)$  and  $trans(O_6)$ ) which differ in the position of oxygen donors of five- and six-coordinted rings are possible. In reaction of this ligand with Co(III) two geometrical isomers (trans( $O_5$ ) and trans(O<sub>5</sub>O<sub>6</sub>)) of hexadentate [Co(eddadp)] have been obtained and resolved [10]. Electronic absorption, circular dichroism (CD) and NMR spectra were used for characterization of these complexes. Circular dichroism spectra of trans(O<sub>5</sub>) and  $trans(O_5O_6)$  isomers have been compared with those for edta-type complexes of known absolute configuration. On the basis of their CD spectra for both isomers of  $[Co(eddadp)]^{-}$  the A absolute configuration have been assigned. The eddadp and S.S. edds ligands (S,S-edds is ethylenediamine-N,N'-disuccinate) have also been used for preparation of the corresponding hexadentate complexes with Cr(III) and Rh(III) ions. In reaction with Cr(III) only  $trans(O_5)$  isomer of hexadentate [Cr(eddadp)]<sup>-</sup> and [Cr(S,S-edds)]<sup>-</sup> complexes have been obtained [11]. Infrared, electronic absorption, and CD spectra were used for characterizing the complexes. The (-)<sub>D</sub>-isomer of the  $trans(O_5)$ -[Cr(eddadp)]<sup>-</sup> complex, having a positive CD peak at the lowest energy in the first spin-allowed d-d absorption band region, is tentatively assigned the  $\Lambda$ configuration, by comparison of its CD spectrum to the corresponding  $trans(O_5)$ and  $trans(O_5)$ -[Cr(S,S-edds)]<sup>-</sup> complexes of known absolute [Co(eddadp)] configuration. The absolute configuration of (-)<sub>D</sub>-Li[Cr(eddadp)].5H<sub>2</sub>O was confirmed by X-ray analyses [12]. In the reaction of RhCl<sub>3</sub> with edadp  $trans(O_5)$  and  $trans(O_5O_6)$ isomers of hexadentate [Rh(eddadp)]<sup>-</sup> have been obtained [13]. The reaction of Rh(III) with stereospecific S.S-edds ligand has also been studied and only  $trans(O_5)$ geometrical isomer of hexadentate  $[Rh(S,S-edds)]^{-1}$  was characterized. IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and electronic absorption spectra have been used for characterization of [Rh(eddadp)]<sup>-</sup> and [Rh(S,S-edds)]<sup>-</sup> complexes. The electronic absorption spectra have also been reported and  $\Lambda$  absolute configuration of [Rh(eddadp)]<sup>-</sup> complexes were assigned by comparison of their CD spectra with those for  $(+)_D$ -trans $(O_5)$ -[Rh(S,S)edds)]<sup>-</sup> of known A absolute configuration [17]. The CD spectrum of  $trans(O_5)$ - $[Rh(S,S-edds)]^{-}$  was also compared with corresponding for  $(-)_{D}$ -isomer of hexadentate [Rh(1,3-pdta)] complex (1,3-pdta is 1,3-propanediaminetetraacetate) and A absolute configuration of the  $[Rh(1,3-pdta)]^{-}$  complex was assigned [18]. The proposed A

absolute configurations for both (-)<sub>D</sub>-isomers of *trans*(O<sub>5</sub>)-Li[Rh(eddadp]<sup>5</sup>H<sub>2</sub>O and [Rh(1,3-pdta)]<sup>-</sup> complexes were confirmed by X-ray analyses [21,25]. The hexadentate Rh(III) and Cr(III) complexes with edtp ligand (edtp is ethylenediaminetetra-3-propionate ion) have been prepared and resolved [26,30]. Infrared, electronic absorption and CD spectra were used for characterization of these complexes. The CD data in the region of *d*-*d* transition are discussed in comparison with those for similar edta-type Rh(III) and Cr(III) complexes of known configuration. For (+)<sub>D</sub> enantiomer of the hexadentate [Rh(edtp)]<sup>-</sup> complex the  $\Lambda$  absolute configuration was assigned by comparison of its CD spectrum with those for Rh(III) edta-type complexes for which absolute configuration are known from X-ray crystallography [21]. The (+)<sub>589</sub>-[Cr(edtp)]<sup>-</sup> complex, having a positive (dominant) CD peak in the first spin-allowed d-d absorption band region, is tentatively assigned the  $\Delta$  configuration [25]. The obtained results have been summarized in a review article written by Radanovic [22]. In this review all papers published in this field until the end of 1982 have also been presented.

Some octahedral chromium(III) complexes of the  $[Cr(N)_2(O)_4]$ -type containing quadridentate ethylenediamine-N,N'-diacetate ligand (edda) with water, hydroxo, oxalato (ox) and malonato (mal) as the additional ligands have been investigated [14-16, 19,20,24]. The  $\alpha$ -cis configurations of the complexes were assigned on the basis of their IR and electronic absorption spectra. These  $\alpha$ -cis configurations were confirmed by X-ray analyses in the case of  $\alpha$ -cis-di- $\mu$ -hydroxobis(ethylenediamine-N,N'diacetato)dichromium(III) tetrahydrate, [Cr(edda)(OH)]<sub>2</sub>4H<sub>2</sub>O [15]. In reactions between quadridentate trimethylenediamine-N,N'-diacetate (tmdda or 1,3-pdda) and ethylenediamine-*N*,*N*'-di-3-propionate (eddp) and chromium(III) ion the two novel hydroxo-dimer chromium(III) complexes were obtained [20]. The electronic absorption and IR spectra were used for characterization of these complexes. It was found that tmdda and eddp ligands prefer the uns-cis configuration, indicating that sixmembered chelate rings have a profound effect on the distribution of geometrical The crystal structure of  $(-)_{589}$ -[Co(en)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)]-*uns-cis*-(-)<sub>546</sub>-[Cr(1,3isomers. pdda)(mal)]H<sub>2</sub>O showed that the six-membered diamine ring assumes the stable chair conformation, the equatorial glycinate ring is puckered, while the axial glycinate ring is in the "envelope" conformation. The  $\Delta\Delta\Delta\Lambda$  absolute configuration of this chromium(III) complex ion was found [32].

Particularly, Radanovic and his coworkers were interested in the study of coordination chemistry of metal(III) ions with pentadentate eda3a-type ligands (ed3a is ethylenediamine-N,N,N'-triacetate ion). Several octahedral cobalt(III) complexes of *cis-eq* geometry containing pentadentate ed3a and monodentate CN<sup>-</sup> ligands, K*cis-eq*-[Co(ed3a)CN] and K*cis-eq*-[Co(med3a)CN] (med3a is *N*-methylethylenediamine-N,N'N'-triacetate ion) and K*trans-eq*-[Co(ed3a)CN] have been prepared and characterized [27]. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of these complexes have been compared with those for [Co(ed3a)(H<sub>2</sub>O)] and [Co(ed3a)((NO<sub>2</sub>)]<sup>-</sup> complexes with the same *cis-eq* geometry. The X-ray crystal structure of the racemic form of NH<sub>4</sub>[Co(ed3a)(CN)]<sup>-</sup>2H<sub>2</sub>O<sup>-</sup>0.5CH<sub>3</sub>OH has been determined and discussed [29].

In continuation of the previous investigation of the transition metal complexes with hexadentate edta-type ligands, new eda3p (ethylenediamine-*N*-acetate-*N*,*N*'*N*'-tri-3-propionate), ed3ap (ethylenediamine-*N*,*N*,*N*'-triacetate-*N*'-3-propionate), *u*-eddadp (ethylenediamine-*N*,*N*-diacetate-*N'*,*N'*-di-3-propionate) and 1,3-pddadp ligands (1,3propanediamine-*N*,*N'*-diacetate-*N*,*N'*-di-3-propionate) have been synthesized [31-33]. These ligands have mixed five- and six-membered chains and in coordination with metal ion different geometrical isomers are possible to obtain. In the reaction of cobalt(III) with eda3p ligand, from two theoretically possible geometrical isomers (*trans*(O<sub>6</sub>) and *trans*(O<sub>5</sub>O<sub>6</sub>)), only *trans*(O<sub>5</sub>O<sub>6</sub>) isomer of hexadentate [Co(eda3p)]<sup>-</sup> complex has been prepared. <sup>1</sup>H NMR, electronic absorption and CD spectra were used to characterize this complex. The (+)<sub>546</sub>-*trans*(O<sub>5</sub>O<sub>6</sub>)-[Co(eda3p)]<sup>-</sup> complex with positive CD peak at lowest energy in the first spin-allowed *d-d* absorption band region is tentatively assigned the A absolute configuration. Study of the reaction of Co(III) with 1,3-pddadp ligand showed that formation of geometrical isomers having the sixmembered glycinate rings in axial position of the octahedral plane was dominant. In this reaction only two *trans*(O<sub>6</sub>) and *trans*(O<sub>5</sub>O<sub>6</sub>) isomers have been characterized. For characterization of these complexes <sup>1</sup>H NMR, <sup>13</sup>C NMR and electronic absorption spectra have been successfully applied [31].

The crystal structures of the octahedral Co(III) and Cr(III) complexes with hexadentate ligand ethylenediamine-N, N, N', N'-tetra-3-propionate (edtp) have been reported [34]. On the basis of X-ray data the  $\Delta$  configuration was established for the isomorphic (+)<sub>589</sub>-Li[Co(edtp)]·3H<sub>2</sub>O and (+)<sub>589</sub>-Li[Cr(edtp)]·3H<sub>2</sub>O enantiomers. The electronic absorption and CD spectra of these complexes were presented and compared with those of other edta-type Co(III) or Cr(III) complexes [34].

The unsymmetrical edta-type ligands: ethylenediamine-N-acetate-N,N'N'-tri-3propionate (eda3p), ethylenediamine-*N*,*N*,*N*'-triacetate-*N*'-3-propionate (ed3ap), ethylenediamine-*N*,*N*-diacetate-*N*',*N*'-di-3-propionate (*u*-eddadp) and 1.3propanediamine-N,N,N'-triacetate-N'-3-propionate (1,3-pd3ap) have been used for preparation of hexadentate Cr(III) [35, 64] and Co(III) [41, 44] complexes. These ligands have mixed carboxylate chains and in coordination with metal ions different geometrical isomers are possible to obtain, except for *u*-eddadp, *vide supra*. In the synthetic reaction of CrCl<sub>3</sub> with ligand eda3p only one  $trans(O_5O_6)$  geometrical isomer of two possible  $(trans(O_5O_6 \text{ and } trans(O_6)))$  has been obtained and resolved into optical isomers [35]. Infrared (IR), electronic absorption and circular dichroism (CD) spectra were used for characterization of the complex. CD data in the region of the d-dtransitions have been discussed in comparison with those of other edta-type Cr(III) complexes of known configuration. The  $(-)_{589}$ -isomer of the *trans* $(O_5O_6)$ - $[Cr(eda3p)]^-$ , having a positive CD peak at lowest energy in the first spin-allowed d-d absorption band region, is tentatively assigned the  $\Lambda$  configuration.

Ethylenediamine-*N*,*N*,*N*'-triacetate-*N*'-3-propionate (ed3ap) on hexadentate coordination can form two possible geometrical isomers:  $trans(O_5)$  and  $trans(O_5O_6)$ . The only one dominant  $trans(O_5)$  isomer has been established in  $[M(ed3ap)]^-$  (M = Co(III) [41, 61] and Cr(III) [64, 65]) complexes. Cobalt(III) complexes with the unsymmetrical hexadentate ligands, ed3ap and *u*-eddadp, have been prepared, chromatographically separated and resolved [41]. The <sup>1</sup>H NMR, electronic absorption and circular dichroism (CD) spectra were used to characterize the complexes. Only one  $trans(O_5)$  geometrical isomer of  $[Co(ed3ap)]^-$  complex was isolated. The enantiomers:  $(-)_{546}$ -trans $(O_5)$ - $[Co(ed3ap)]^-$  and  $(+)_{546}$ - $[Co(u-eddadp)]^-$  with a positive CD peak at lowest energy in the first spin-allowed absorption band region are

tentatively assigned the  $\Lambda$  absolute configuration. The  $\Lambda$  absolute configuration of  $(-)_{546}$ -*trans*(O<sub>5</sub>)-[Co(ed3ap)]<sup>-</sup> was confirmed by X-ray crystallography [61].

Chromium(III) complexes with ed3ap and *u*-eddadp ligands also have been prepared, chromatographically separated and characterized [64]. IR, deuteron NMR (<sup>2</sup>H NMR), magnetic circular dichroism (MCD) and electronic absorption spectra were used to characterize the complexes. Only one *trans*(O<sub>5</sub>) of two geometrical isomers of  $[Cr(ed3ap)]^-$  complex was isolated. The structures of both *trans*(O<sub>5</sub>)-[Cr(ed3ap)]<sup>-</sup> and  $[Cr(u-eddadp)]^-$  complexes have been determined by X-ray crystallography [65]. The *trans*(O<sub>5</sub>)-[Cr(ed3ap)]<sup>-</sup> complex have been resolved and its CD spectrum was compared with those for similar edta-type Cr(III) complexes. The (-)<sub>589</sub>-isomer of the *trans*(O<sub>5</sub>)-[Cr(ed3ap)]<sup>-</sup>, with a positive CD peak at the lowest energy in the first spinallowed *d-d* absorption band region, is assigned the  $\Lambda$  configuration. The absolute configuration of this complex was also confirmed by X-ray analysis.

Ligand 1,3-propanediamine-N,N,N'-triacetate-N'-3-propionate (1,3-pd3ap) differs from ed3ap only in the length of diamine chain, thus theoretically possible geometrical isomers that these ligands may form on hexadentate coordination are the same. The only one geometrical isomer (*trans*(O<sub>5</sub>O<sub>6</sub>)) of the hexadentate Co(III) complex with 1,3-pd3ap has been prepared and resolved [44]. The NMR, electronic absorption and circular dichroism (CD) spectra were used to characterize the complex. The (-)<sub>546</sub>-isomer of the *trans*(O<sub>5</sub>O<sub>6</sub>)-[Co(1,3-pd3ap)]<sup>-</sup>, with a positive CD peak at lowest energy in the first spin-allowed absorption band region is tentatively assigned the A absolute configuration.

The symmetrical ligand 1,3-propanediamine-*N*,*N*'-diacetate-*N*,*N*'-di-3propionate (1,3-pddadp) has been used for preparation of hexadentate Co(III) [40] and Rh(III) [42] complexes. Possible geometrical isomers that may be obtained in the synthetic reactions of 1,3-pddadp with metal ions are the same as those for eddadp ligand (*vide supra*). In reaction of this ligand with Co(III) ion two geometrical isomers (*trans*(O<sub>5</sub>O<sub>6</sub>) and *trans*(O<sub>6</sub>)) of hexadentate [Co(1,3-pddadp)]<sup>-</sup> complex have been obtained and resolved [40]. Electronic absorption, circular dichroism (CD) and NMR spectra were used for characterization of these complexes. The (+)<sub>546</sub>-*trans*(O<sub>5</sub>O<sub>6</sub>)-[Co(1,3-pddadp)]<sup>-</sup> and (+)<sub>546</sub>-*trans*(O<sub>6</sub>)-[Co(1,3-pddadp)]<sup>-</sup> enantiomers with a positive CD peak at lowest energy in the first spin-allowed *d-d* absorption band region are tentatively assigned the A absolute configuration.

The *trans*( $O_6$ ) geometry of [Co(1,3-pddadp)]<sup>-</sup> also have been established in the crystal structure of racemate Ktrans(O<sub>6</sub>)-[Co(1,3-pddadp)]·3H<sub>2</sub>O [50] as well as in the crystal structures of optically pure compounds:  $K_{1/2}(H_5O_2)_{1/2}\{(-)_D - trans(O_6) - [Co(1,3$ pddadp)]} $\cdot 2H_2O$  [63] and Li{(-)<sub>D</sub>-trans(O<sub>6</sub>)-[Co(1,3-pddadp)]} $\cdot 7H_2O$  [63]. The crystallographic studies of cobalt(III) amine carboxylates were of particular interest in connection with the mystery of hydronium ions of different kinds [63]. It has been established that minor variations in composition and/or stereochemistry of the cobalt amine carboxylates are sufficient to influence the crystallization of hydronium ion or potassium-hydronium evidenced mixed salts as in crystal structure of  $K_{1/2}(H_5O_2)_{1/2}\{(-)_D - trans(O_6) - [Co(1, 3 - pddadp)]\} \cdot 2H_2O.$ 

In the reaction of  $RhCl_3$  with 1,3-pddadp ligand two geometrical isomers (*trans*(O<sub>5</sub>) and *trans*(O<sub>5</sub>O<sub>6</sub>)) of hexadentate  $[Rh(1,3-pddadp)]^-$  complex have been prepared, resolved into the optical isomers and characterized [42, 70]. Electronic

absorption, circular dichroism (CD) and NMR spectra were used for characterization of these complexes. For both geometrical isomers X-ray data were reported [70]. The electronic absorption and CD spectra were compared with those for similar edta-type Rh(III) complexes. The optical isomers of the [Rh(1,3-pddadp)]<sup>-</sup> complex ((-)<sub>589</sub>*trans*(O<sub>5</sub>) and (+)<sub>589</sub>-*trans*(O<sub>5</sub>O<sub>6</sub>)) exhibited similar CD splitting and sign patterns in the region of the lower energy absorption band (a lowest energy positive CD peak followed by a negative one). Both optical isomers were assigned the  $\Lambda$  absolute configuration. The assignment was confirmed by X-ray analysis in the case of  $\Lambda$ -(+)<sub>589</sub>-*trans*(O<sub>5</sub>O<sub>6</sub>)-[Rh(1,3-pddadp)]<sup>-</sup>. Earlier reported [Rh(1,3-pdta)]<sup>-</sup> [18, 21] and [Rh(edtp)]<sup>-</sup> [26] complexes exhibiting opposite alternating CD sign pattern have also been assigned the  $\Lambda$  configuration.

The results obtained in studies of stereochemistry and optical activity of edtatype complexes of Co(III), Cr(III) and Rh(III) until 1993 have been summarized in the review article [43].

In the last decade, his research was extended on sterechemistry of nickel(II) and copper(II) complexes with edta-type and related ligands. The X-ray data reported for these complexes formed the firm basis for the stereochemical study.

The hexadentate ligands: 1,3-pddadp, 1,3-pdta, edtp and ed3ap have been used for preparation of the corresponding copper(II) complexes [54,56,57,66,67,69]. In the synthetic reactions of Cu(II) ion with 1,3-pddadp ligand only one favored  $trans(O_6)$ isomer was obtained [54,56]. Two tetragonally elongated octahedral complexes:  $trans(O_6)$ -[Cu(H<sub>2</sub>1,3-pddadp)]·1.5H<sub>2</sub>O and  $trans(O_6)$ -Na<sub>2</sub>[Cu(1,3pddadp)]·NaNO<sub>3</sub>·2H<sub>2</sub>O have been prepared and characterized. IR and electronic absorption spectra were used for characterizing the complexes and the X-ray data have been reported for both 1,3-pddadp complexes of Cu(II). The study of reaction of Cu(II) ion with unsymmetrical ed3ap ligand showed that formation of the geometrical isomer having the five-membered glycinate rings in axial positions of the octahedral plane was favored [67]. In this reaction only one trans(O<sub>5</sub>) geometrical isomer of  $[Cu(ed_{3ap})]^{2-}$  complex was obtained and characterized by IR and electronic absorption spectroscopy. The extent of axial elongation in  $trans(O_5)$ -[Cu(ed3ap)]<sup>2-</sup> as well as in  $[Cu(1,3-pdta]^{2-}[66]]$  complex was found to be restricted by axially coordinated fivemembered glycinate rings. The X-ray analyses for both complexes have been reported and the stereochemistry of tetragonal octahedral Cu(II)-edta-type complexes has been discussed in relation to the structure of ligand and geometry of the complex.

In reaction of  $CuCl_2$  with hexadentate ligand ethylenediamine-*N*,*N*,*N'*,*N'*-tetra-3propionate (edtp) capable of forming only six-membered carboxylato rings squrebased pyramidal complex was obtained [57,69]. IR and electronic absorption spectra were used to characterize the complex. A square-based pyramidal geometry was established by X-ray crystallography for Mg[Cu(edtp)]·10H<sub>2</sub>O and structural parameters describing distortion of five-coordinate [Cu(edtp)]<sup>2–</sup> complex ion were compared with those for similar copper(II) complexes with edta-type and related ligands. However, for Rh(III) Co(III) and Cr(III) complexes with the same edtp ligand, octahedral geometry was established, *vide supra*.

The quadridentate edda-type ligands forming six-membered rings: 1,3propanediamine-N,N'-diacetate (1,3-pdda) and ethylenediamine-N,N'-di-3-propionate (eddp) have also been used for syntheses of Ni(II) and Cu(II) complexes. Two paramagnetic octahedral nickel(II) complexes:  $[Ni(1,3-pdda)(H_2O)_2]$  and  $[Ni(eddp)(H_2O)_2]\cdot H_2O$  have been prepared and characterized by IR and electronic absorption spectroscopy [48]. For both complexes uns-*cis* geometry was proposed and in the case of  $[Ni(1,3-pdda)(H_2O)_2]$  it was confirmed by X-ray analysis. With the same quadridentate 1,3-pdda and eddp ligands two square-based pyramidal copper(II) complexes have been prepared and characterized by IR and electronic absorption spectroscopy [58]. Crystallographic data were reported for both  $[Cu(1,3-pdda)(H_2O)]$  and  $[Cu(eddp)(H_2O)]\cdot 3.5H_2O$  complexes and compared with those of similar five-coordinate copper(II) complexes.

In the synthetic reactions of Ni(II) ion with hexadentate eddadp and edtp ligands two paramagnetic octahedral complexes ( $[Ni(eddap)]^{2-}$  and  $[Ni(edtp)]^{2-}$ ) have been prepared and characterized [60]. The IR and electronic absorption spectra were used for characterizing the complexes. Due to the less strain in axial glycinate rings, only one (*trans*(O<sub>5</sub>)) of three geometrical isomers of the  $[Ni(eddadp)]^{2-}$  complex have been isolated. This dominant geometry has been established by X-ray analysis. Hexadentate 1,3-pddadp ligand also has been used for the preparation of Ni(II) complexes. This ligand differs from eddadp only in the length of diamine chain and in reaction with Ni(II) ion two geometrical isomers (*trans*(O<sub>5</sub>) and *trans*(O<sub>5</sub>O<sub>6</sub>)) of hexadentate  $[Ni(1,3-pddadp)]^{2-}$  complex have been obtained and characterized [71]. Infrared and electronic absorption spectra were used for characterization of these complexes. The *trans*(O<sub>5</sub>) geometry of octahedral  $[Ni(1,3-pddadp)]^{2-}$  complex was confirmed by X-ray analysis.

In the simple synthetic reactions of M(II) sulfates (M(II) = Cu, Ni, Co) with Ba[Ba(1,3-pdta)]·2H<sub>2</sub>O the isomorphic series  $[M'^{II}(H_2O)_6[M^{II}(1,3-pdta)]·2H_2O$  was obtained [66,68,72]. IR and electronic absorption spectra were used to characterize these complexes. The crystallographic data of  $[M'^{II}(H_2O)_6[M^{II}(1,3-pdta)]·2H_2O$  (M'(II) = Mg and M(II) = Cu [66]; M'(II) = Mg and M(II) = Ni [68]; and M'(II) = Mg or Co and M(II) = Co ) complexes have been reported and compared with those for similar edta-type complexes.

## 2. Scientific papers of Dušan J. Radanović

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    M. B. Ćelap, T. J. Janić and D. J. Radanović
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lead, copper, cadmium, uranium, iron and zinc by precipitation
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Study of the reactions of hexanitrocobaltates(III) with amino acids. II.
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Inorg. Chem., 4 (1965) 1494-1495.
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Study of the reactions of hexanitrocobaltate(III) with amino acids. III
Syntheses of dinitrodiglycinatocobaltate(III) with amino acids. III
Syntheses of dinitrodiglycinatocobaltate(III) from complex cobaltic
compounds of the diamine, triamine, tetraamine, pentaamine and hexaamine
types
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