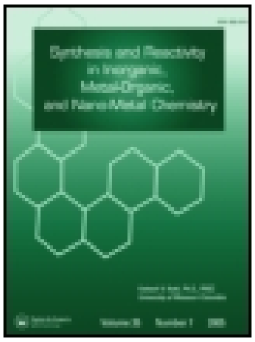

Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

ISSN: 0094-5714 (Print) 1532-2440 (Online) Journal homepage: http://www.tandfonline.com/loi/lsrt19

Synthesis and Characterization of Sym-Cis- and Unsym-Cis-(Ethylenediamine-N, N'-Di-3-Propionato)Cobalt(Iii) Complexes with Symmetrical N, N'-Substituted Diamines

Sanja R. Grguric & Tibor J. Sabo

To cite this article: Sanja R. Grguric & Tibor J. Sabo (1999) Synthesis and Characterization of Sym-Cis- and Unsym-Cis-(Ethylenediamine-N, N'-Di-3-Propionato)Cobalt(Iii) Complexes with Symmetrical N, N'-Substituted Diamines, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 29:9, 1567-1578, DOI: 10.1080/00945719909351719

To link to this article: http://dx.doi.org/10.1080/00945719909351719

SYNTH. REACT. INORG. MET.-ORG. CHEM., 29(9), 1567–1578 (1999)

SYNTHESIS AND CHARACTERIZATION OF *SYM-CIS*- AND *UNSYM-CIS*-(ETHYLENEDIAMINE-*N,N'*-DI-3-PROPIONATO)COBALT(III) COMPLEXES WITH SYMMETRICAL *N,N'*-SUBSTITUTED DIAMINES

Sanja R. Grgurić and Tibor J. Sabo*

Faculty of Chemistry, University of Belgrade, P. O. Box 158,
11001 Belgrade, Yugoslavia

ABSTRACT

A series of octahedral *sym-cis* and *unsym-cis* cobalt(III) complexes involving tetradentate ethylenediamine-*N,N'*-di-3-propionate ion (eddp) and symmetrical diamines, [ethylenediamine (en), *N,N'*-dimethylethylenediamine (dmen) and *N,N'*-diethylethylenediamine (deen)] were prepared by reaction of sodium *unsym-cis*-(ethylenediamine-*N,N'*-di-3-propionato)(carbonato)cobaltate(III) dihydrate with the corresponding diamine. The stereochemistry of the complexes prepared was investigated through ion-exchange chromatography, electronic absorption, infrared and ^{1}H NMR spectroscopy.

INTRODUCTION

Geometrical isomerism in metal complexes of linear flexibile tetradentate ligands having the donor atom array ONNO such as edda (ethylenediamine-*N,N'*-diacetate ion) or eddp (ethylenediamine-*N,N'*-di-3-propionate ion) has been an interesting field studied by a number of authors[1-5]. Such ligands can occupy four of the octahedral sites around a Co(III) ion and the other two sites may be occupied by other ligands, in which two geometrical isomers are possible, as shown in Fig. 1.

The eddp complexes were obtained only in the *unsym-cis* geometry except for the ethylenediamine complex[6,7], while the edda complexes have been isolated in both geometries, *sym-cis* and *unsym-cis*[1]. It was noted that the complexes containing eddp, which forms a six-membered amino-carboxylato backbone, prefer the *unsym-cis* configuration, suggesting that the size of the chelate ring has a profound effect on the distribution of geometric isomers[2]. We have now succeeded in synthesizing sufficient quantities of *sym-cis* and *unsym-cis* isomers of eddp-Co(III) to permit a stereochemical investigation.

We report here our continuing study of the cobalt(III) complexes of edda-type ligands, the synthesis of *sym-cis* and *unsym-cis* isomers of (ethylenediamine-*N,N'*-di-3-propionato)cobalt(III) with symmetrical diamines, *N,N'*-dimethylethylenediamine (dmen) and *N,N'*-diethylethylenediamine (deen). Also, we have prepared a previously synthesized *unsym-cis*-(ethylenediamine-*N,N'*-di-3-propionato)ethylenediaminecobalt(III) complex by a new route (substitution reaction). The geometric configurations of the isolated complexes are assigned on the basis of their electronic absorption, infrared and ^{1}H NMR spectroscopy.

RESULTS AND DISCUSSION

For the preparation of the eddp-Co(III) complexes containing diamines, *unsym-cis*-(ethylenediamine-*N,N'*-di-3-propionato)(carbonato)cobaltate(III) ion was used as a starting material. Although it is well known that the eddp ligand prefers the *unsym-cis* configuration, the *sym-cis* isomers were obtained, too.

sym-cis *unsym-cis*

Fig. 1. Possible Geometrical Isomers of the $[Co(eddp)diamine]^+$ Complexes

Under the reaction conditions used in the present syntheses, the eddp chelate inhibits the isomerization of the complex even when the carbonate is displaced and leads to partial retention of geometry on going from the carbonato to diamine complexes. Partial isomerization of geometry during the synthesis can be envisioned due to greater non-bonding interactions between eddp and additional diamine when the geometry is *unsym-cis*[8].

The complexes prepared and characterized in this study are *unsym-cis*-[Co(eddp)en]Cl, *sym-cis*-[Co(eddp)dmen]Cl, *unsym-cis*-[Co(eddp)dmen]Cl, *sym-cis*-[Co(eddp)deen]Cl and *unsym-cis*-[Co(eddp)deen]Cl:

$$\textit{unsym-cis}\text{-}Na[Co(eddp)CO_3] + \text{diamine} + 2HCl \rightarrow$$
$$\textit{unsym-cis}\text{-} + \textit{sym-cis}\text{-}[Co(eddp)\text{diamine}]Cl + NaCl + H_2O + CO_2$$

The *sym-cis* isomers are purple and *unsym-cis* isomers are red-purple. The order of column elution of the isomers is first *sym-cis* and then *unsym-cis* which is consistent with the greater effective dipole moment expected for the *unsym-cis* isomer[8,9] and is consistent with the earlier work[6].

Electronic Absorption Spectra

The *unsym-cis* isomers are readily distuinguished from the *sym-cis* isomers on the basis of their electronic absorption spectra. The electronic absorption spectra of the *sym-cis* and *unsym-cis* isomers of the [Co(eddp)diamine]$^+$ complexes are shown in Fig. 2 and their corresponding maxima are listed in Table I. It is well known experimentally and theoretically that *trans*-(O)-[Co(N_4O_2)] type complexes exhibit large splitting of the first absorption band, while for *cis*-(O)-[Co(N_4O_2)] type complexes this band is nearly symmetrical because of the smaller splitting[10]. The electronic absorption spectra of the investigated complexes show big differences in the shape of the band of the lower energy spin-allowed transition (Fig. 2). The purple isomer clearly shows band splitting and was assigned the *sym-cis* geometry; the red-purple isomer exhibits a symmetrical band and was assigned the *unsym-cis* geometry. In a previous paper[1], it was reported that complexes with coordinated *sym-cis* edda-type tetradentates have the maximum of the first absorption band at a longer wave length than the corresponding *unsym-cis* isomer. Our results confirm these facts (Fig. 2, Table I).

The extinction coefficients of the absorption band maxima for the *unsym-cis* complexes are larger than for the corresponding *sym-cis* isomers. This fact is consistent with the lower symmetry of the *unsym-cis* isomer. Table I also shows the shift of the first absorption band to lower energy as the hydrogen on the nitrogens on ethylenediamine are progressively substituted by methyl (dmen) and ethyl (deen). This shift is probably due to lengthening of metal-ligand bonds to accommodate the *N*-substituted alkyl groups.

Infrared Spectra

The important IR data for the *sym-cis* and *unsym-cis* isomers of the presently investigated [Co(eddp)diamine]$^+$ complexes are given in Table II.

All of the complexes showed a strong absorption around 1600 cm^{-1}, the CO-asymmetric stretching region. The lack of absorption between 1700-1800 cm^{-1} indicates that the carboxyl groups of eddp definitely are coordinated to the central cobalt(III) ion[12]. The more complicated shape in the carboxylate region of the *unsym-cis* isomers than the corresponding *sym-cis* isomers of the

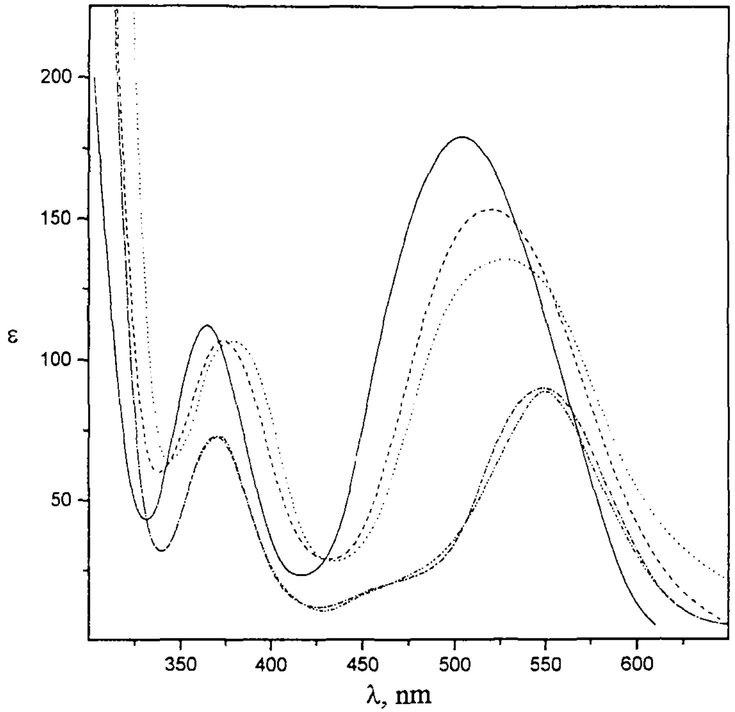

Fig. 2. Electronic Absorption Spectra of *unsym-cis*-[Co(eddp)en]$^+$ (——), *sym-cis*-[Co(eddp)dmen]$^+$ (·-·-·-), *unsym-cis*-[Co(eddp)dmen]$^+$ (------), *sym-cis*-[Co(eddp)deen]$^+$ (-·-·-·) and *unsym-cis*-[Co(eddp)deen]$^+$ (········)

Table I

Band Maxima in the Visible Spectra of Some [Co(edda)L]$^+$ Complexes[a]

Complex	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3	Ref.
sym-cis-[Co(edda)en]$^+$	528	87.3	449	sh	364	113	8
unsym-cis-[Co(edda)en]$^+$	493	170			359	169	11
sym-cis-[Co(eddp)en]$^+$	542	93	455	33	362	81	6
unsym-cis-[Co(eddp)en]$^+$	508	218			367	120	
sym-cis-[Co(eddp)dmen]$^+$	550	95	465	sh	370	75	this work
unsym-cis-[Co(eddp)dmen]$^+$	520	160			373	110	
sym-cis-[Co(eddp)deen]$^+$	550	93	470	sh	370	75	
unsym-cis-[Co(eddp)deen]$^+$	521	140			379	110	

[a] Wave length (λ) in nm. Extinction coefficient (ε) in mol^{-1}dm^{3}cm^{-1}.
L represents a bidentate ligand

Table II

Characteristic IR Bands (cm^{-1}) of the Complexes

Complex	$\nu(NH_2)$	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$
unsym-cis-[Co(eddp)en]$^+$	3431 vs	1592 vs	1396 vs
sym-cis-[Co(eddp)dmen]$^+$	3435 s	1597 vs	1392 s
unsym-cis-[Co(eddp)dmen]$^+$	3436 s	1608 s	1398 m
sym-cis-[Co(eddp)deen]$^+$	3432 vs	1603 vs	1402 s
unsym-cis-[Co(eddp)deen]$^+$	3436 s	1607 s	1401 s

[Co(eddp)diamine]$^+$ complexes is consistent with their lower molecular symmetry. The symmetric stretching bands of the coordinated carboxylate groups lie in the expected region (about 1400 cm^{-1}). The stretching bands of the amino groups are also summarized in Table II.

^{1}H NMR Spectra

^{1}H NMR has been used extensively in the characterization of metal chelates containing aminocarboxylate ligands[13-15]. Consistent with the above papers, *sym-cis* isomers of the dmen and deen complexes showed an AA'BB' pattern at δ 2.8 to 3.5 due to the protons of the β-alaninato ring of eddp ligand. Protons associated with the N-CH_2-CH_2-N ring of both eddp and diamines are found between δ 2.1 and 2.8. This protons exhibit an AA'BB' pattern owing to the different chemical shifts of axial and equatorial protons. Because of the highly collapsed nature and the overlap of the patterns, a complete analysis is very difficult. In the *unsym-cis* isomers, asymmetry introduced by changing one of the R β-alaninato ring[16] (oxygen above the plane containing Co and eddp nitrogens) to a G ring (oxygen in Co-eddp nitrogen plane) should result in two different patterns. The *unsym-cis* isomers exhibit more complex spectra in this region where intense peaks are observed at δ 3.08 and 3.00 for the dmen and deen complexes, respectively. These are superimposed on the same type of AA'BB' pattern found in the *sym-cis* isomers. The dmen methyl resonance centered at δ 2.43 for the *sym-cis* isomer, is split into a doublet at δ 2.13 and 2.25 for the *unsym-cis* isomer. The deen the methyl resonance is centered at δ 1.15 and 1.30 for *sym-cis* and *unsym-cis* isomers, respectively, and pattern is much more complicated for the latter isomer. The $-CH_2-$ resonance of the deen ethyl groups is complex and overlaps with AA'BB' patterns.

EXPERIMENTAL

Materials

Sodium *unsym-cis*-(ethylenediamine-*N*,*N'*-di-3-propionato)(carbonato)cobaltate(III) dihydrate was prepared using a previously described procedure[2]. Other reagents were obtained commercially and used without further purification.

Preparation of *unsym-cis*-(Ethylenediamine-*N*,*N'*-di-3-propionato)(Ethylenediamine)cobalt(III) Chloride, [Co(eddp)(en)]Cl

To a solution of 0.38 g (1 mmol) of *unsym-cis*-$Na[Co(eddp)CO_3]\cdot 2H_2O$ in 10.0 mL of water, 0.95 mL (1.5 mmol) of a 10% aqueous ethylenediamine solution was added, and the pH of the solution adjusted to 8.5 with 0.2 molar HCl. After heating with stirring for 2 h at 50° C, the solution was concentrated to 5.0 mL and placed onto a 2.5 x 30 cm column containing Sephadex G-10. The red-violet eluate was then poured onto a 2.5 x 32 cm column containing SP-Sephadex C-25. The column was washed with water to remove the non-adsorbed starting complex and then eluted with 0.2 molar KCl. The adsorbed complex separated into two bands, a purple band (trace amount), and a slower moving red-purple band. The eluate of the red-purple band was concentrated under reduced pressure. Then methanol was added in order to remove KCl.

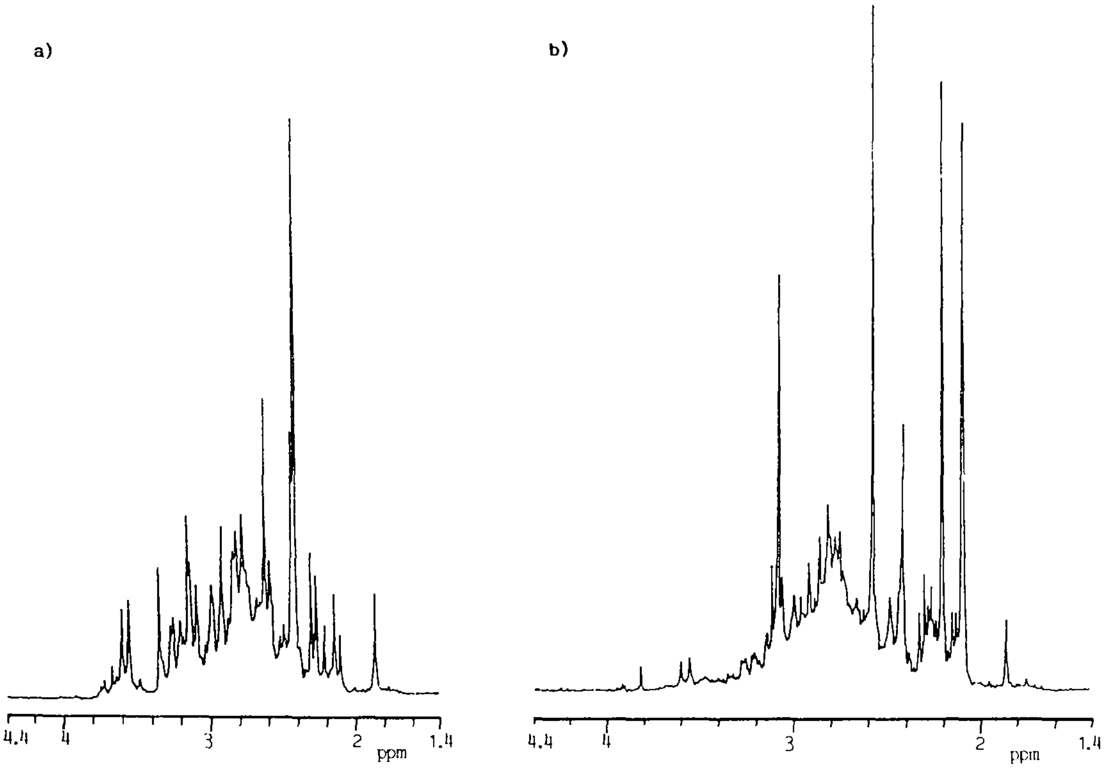

Fig. 3. ^{1}H NMR Spectra of a) *sym-cis*-[Co(eddp)dmen]$^+$, b) *unsym-cis*-[Co(eddp)dmen]$^+$

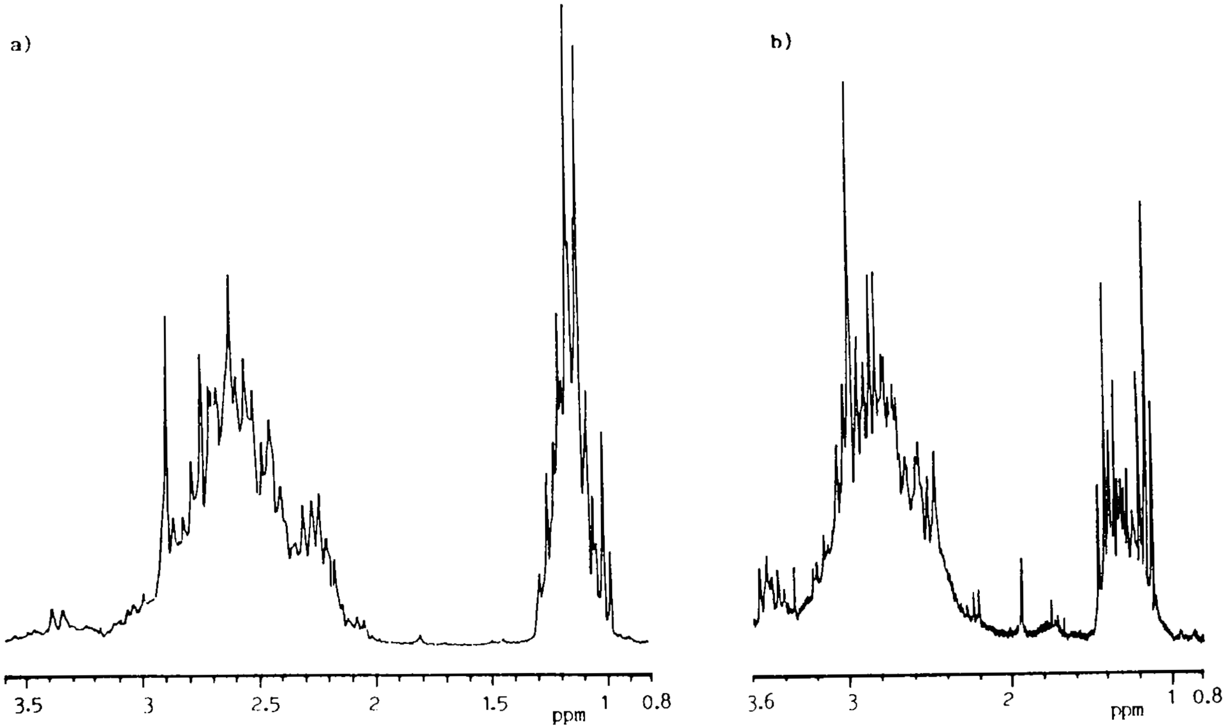

Fig. 4. ^{1}H NMR Spectra of a) *sym-cis*-[Co(eddp)deen]$^+$, b) *unsym-cis*-[Co(eddp)deen]$^+$

From the desalted solution *unsym-cis*-[Co(eddp)(en)]Cl complex was obtained. Yield: 0.17 g (39.5%) *Anal.* calc. for *unsym-cis*-[Co(eddp)(en)]Cl·4H_2O ($C_{10}H_{30}ClCoN_4O_8$) (MW 428.82): C, 28.00; H, 7.06; N, 13.06%. Found: C, 27.98; H, 7.15; N, 12.78 %. Decomposition point: 180° C.

Preparation of *sym-cis* and *unsym-cis*-(Ethylenediamine-*N,N'*-di-3-propionato)(*N,N'*-dimethylethylenediamine)cobalt(III) Chloride, [Co(eddp)(dmen)]Cl

To a solution of 0.38 g (1 mmol) of *unsym-cis*-Na[Co(eddp)CO_3]·2H_2O in 10.0 mL of water, 1.45 mL (1.5 mmol) of a 10% aqueous *N,N'*-dimethylethylenediamine solution was added, and the pH of the solution adjusted to 9 with 0.2 molar HCl. After heating with stirring for 2 h at 50° C, the solution was concentrated to 5.0 mL and placed onto a 2.5 x 30 cm column containing Sephadex G-10. The red-violet eluate was then poured onto a 2.5 x 32 cm column containing SP-Sephadex C-25. The column was washed with water to remove the non-adsorbed starting complex and then eluted with 0.2 molar KCl. The adsorbed complex separated into two bands, a purple band, and a slower moving red-purple band. Each eluate of the purple and red-purple band was concentrated under reduced pressure. Then methanol was added in order to remove KCl. The chloride salts of *sym-cis*- and *unsym-cis*-[Co(eddp)(dmen)]$^+$ were obtained from the desalted purple and red-purple solutions, respectively. Yield: 0.03 g (7.14%) of purple-red (*sym-cis*) and 0.13 g (29.54%) of red (*unsym-cis*) isomer. *Anal.* calc. for *sym-cis*-[Co(eddp)(dmen)]Cl·2H_2O ($C_{12}H_{30}ClCoN_4O_6$) (MW 420.84): C, 34.24; H, 7.20; N, 13.32%. Found: C, 33.96; H, 7.58; N,13.64%. Decomposition point: 176° C. Calc. for *unsym-cis*-[Co(eddp)(dmen)]Cl·3H_2O ($C_{12}H_{32}ClCoN_4O_7$) (MW 438.86): C, 32,84; H, 7.36; N, 12.77%. Found: C, 32.40; H, 7.48; N, 12.89 %. Decomposition point: 176° C.

Preparation of *sym-cis-* and *unsym-cis-*(Ethylenediamine-*N*,*N'*-di-3-propionato)(*N*,*N'*-diethylethylenediamine)cobalt(III) Chloride, [Co(eddp)(deen)]Cl

Using 0.38 g (0.1 mmol) of *unsym-cis*-Na[Co(eddp)CO$_3$]·2H$_2$O and 1.95 mL (1.5 mmol) of a 10% aqueous solution of *N*,*N'*-diethylethylenediamine, the complexes were obtained in the same manner as described above. Yield: 0.07 g (16.1%) of purple-red (*sym-cis*) and 0.10 g (22.7%) of red (*unsym-cis*) isomer. *Anal.* calc. for *sym-cis*-[Co(eddp)(deen)]Cl·1.5H$_2$O (C$_{14}$H$_{33}$ClCoN$_4$O$_{5.5}$) (MW 439.89): C, 38.22; H, 7.57; N, 12.74%. Found: C, 38.10; H,7.15; N,12.68 %. Decomposition point: 164° C. Calc. for *unsym-cis*-[Co(eddp)(deen)]Cl·1.5H$_2$O (C$_{14}$H$_{33}$ClCoN$_4$O$_{5.5}$) (MW 439.89): C, 38.22; H, 7.57; N, 12.74%. Found: C, 37.92; H, 8.03; N,12.97 %. Decomposition point: 167° C.

Analytical Methods

Infrared spectra were recorded on a Perkin-Elmer FTIR 31725-X spectrophotometer using the KBr pellet technique. Electronic absorption spectra were recorded on a Varian GBC 911A spectrophotometer. Aqueous $1 \cdot 10^{-3}$ molar solutions of the complexes were used for these measurements. ^{1}H NMR spectra were recorded on a Varian Gemini-200 NMR spectrometer using DSS [sodium salt of 3-(trimethylsilyl)propanesulfonic acid] as internal reference in D$_2$O. Elemental microanalyses for C, H, N were performed by standard methods.

ACKNOWLEDGMENT

The authors are grateful to the Ministry of Science and Technology of the Republic of Serbia for financial support.

REFERENCES

1. D. J. Radanović, Coord. Chem. Rev., 54, 159 (1984).

2. D. J. Radanović, M. I. Djuran, V. D. Miletić and R. R. Parijez, J. Serb. Chem. Soc., 50, 99 (1985).

3. T. J. Sabo, S. R. Grgurić, D. M. Minić and S. R. Trifunović, J. Coord. Chem., 44, 173 (1998).

4. S. R. Grgurić, S. R. Trifunović and T. J. Sabo J. Serb. Chem. Soc., 63, 669 (1998).

5. T. J. Sabo, S. R. Grgurić, Ž. Lj. Tešić and S. R. Trifunović, J. Serb. Chem. Soc., 63, 195 (1998).

6. H. Kawaguchi, N. Maruyama, T. Ama and T. Yasui, Bull. Chem. Soc. Jpn., 65, 175 (1992).

7. N. Sakagami, T. Yasui, H. Kawaguchi, T. Ama, S. Kaizaki, Bull. Chem. Soc. Jpn., 67, 680 (1994).

8. J. I. Legg and D.W. Cooke, Inorg. Chem., 4, 1576 (1965).

9. E. L. King and R. R. Walters, J. Am. Chem. Soc., 74, 4471 (1952).

10. K. D. Gailey, K. Igi and B. E. Douglas, Inorg. Chem., 14, 2956 (1975).

11. L. J. Halloran and J. I. Legg, Inorg. Chem., 13, 2193 (1974).

12. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", Wiley, New York (1986)

13. P. J. Garnett and D. W. Watts, Inorg. Chim. Acta, 8, 293 (1974).

14. P. F. Coleman, J. I. Legg and J. Steele, Inorg. Chem., 9, 937 (1970).

15. J. L. Sudmeier and G. Occupati, Inorg. Chem., 7, 2524 (1968).

16. H. A. Weakliem and J. L. Hoard, J. Am. Chem. Soc., 81, 549 (1959).

Received: 11 March 1999
Accepted: 7 June 1999

Referee I: M. T. Caudler
Referee II: J. H. Worrell