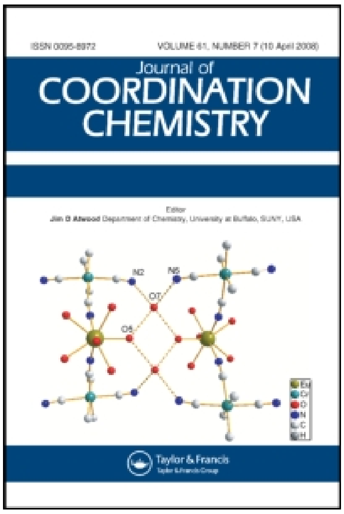

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

PREPARATION AND CHARACTERIZATION OF COBALT(III) COMPLEXES WITH SARCOSINE AND SOME TETRADENTATE LIGANDS OF THE EDDA TYPE

Vesna M. Đinović[a]; Sanja R. Grgurić[a]; Xu Xing-You[b]; Tibor J. Sabo[a]
[a] Faculty of Chemistry, University of Belgrade, Belgrade, Yugoslavia [b] Dept. of Chemical Engineering, Huihai Institute of Technology, Lianyugang, Jingsu, P.R. China

To cite this Article Đinović, Vesna M. , Grgurić, Sanja R. , Xing-You, Xu and Sabo, Tibor J.(2001) 'PREPARATION AND CHARACTERIZATION OF COBALT(III) COMPLEXES WITH SARCOSINE AND SOME TETRADENTATE LIGANDS OF THE EDDA TYPE', Journal of Coordination Chemistry, 53: 4, 355 — 363

To link to this Article: DOI: 10.1080/00958970108022622

URL: http://dx.doi.org/10.1080/00958970108022622

J. Coord. Chem., 2001, Vol. 53, pp. 355–363
Reprints available directly from the publisher
Photocopying permitted by license only

PREPARATION AND CHARACTERIZATION OF COBALT(III) COMPLEXES WITH SARCOSINE AND SOME TETRADENTATE LIGANDS OF THE EDDA TYPE

VESNA M. ĐINOVIĆ[a], SANJA R. GRGURIĆ[a], XU XING-YOU[b]
and TIBOR J. SABO[a,*]

[a]*Faculty of Chemistry, University of Belgrade, P.O. Box 158, 11001 Belgrade, Yugoslavia;* [b]*Dept. of Chemical Engineering, Huihai Institute of Technology, Lianyugang, Jingsu, 222005 P.R. China*

(Received 1 June 2000)

Meridional geometrical isomers of cobalt(III) complexes with sarcosine (*N*-methylglycine) and tetradentate ligands edda (ethylenediamine-*N*,*N'*-diacetate ion), eddp (ethylenediamine-*N*,*N'*-di-3-propionate ion) and 1,3-pdda (1,3-propylenediamine-*N*,*N'*-diacetate ion) have been prepared. The edda and eddp cobalt(III) complexes were made by the reaction of sarcosine and sodium ethylenediamine-*N*,*N'*-diacetato(carbonato)cobaltate(III), and sodium *uns-cis*-(ethylenediamine-*N*,*N'*-di-3-propionato)(carbonato)cobaltate(III) dihydrate, respectively. The previously synthesized pdda-cobalt(III) complex with sarcosine was obtained by a new route by direct synthesis of cobalt(II) chloride hexahydrate with sarcosine and 1,3-pdda in the presents of lead(IV) oxide. Complexes were isolated chromatographically and characterized by elemental analysis, electron absorption spectra, infrared spectra and ^{1}H NMR spectroscopy.

Keywords: Cobalt (III) complexes; Edda type ligands; Sarcosine

INTRODUCTION

Ethylenediamine-*N*,*N'*-di-3-propionate (eddp) and 1,3-propylenediamine-*N*,*N'*-diacetate (1,3-pdda) are tetradentate ligands similar to edda (edda = ethylenediamine-*N*,*N'*-diacetate ion). Metal(III) complexes with

---

[*] Corresponding author.

edda type ligands have been widely investigated [1–14]. Such ligands can occupy four octahedral sites around a central ion and the other two sites may be occupied by other ligands. In the case of (edda-type)M(III) complexes with symmetrical bidentate ligands (such as oxalate or ethylenediamine) two geometrical isomers can be expected, *s-cis* and *uns-cis* (Fig. 1). However, for (edda-type)M(III) complexes with unsymmetrical bidentate ligands (such as glycine) three geometrical isomers are theoretically possible, *s-cis*, *fac-uns-cis* and *mer-uns-cis* (Fig. 1).

Amino acids, as unsymmetrical bidentate ligands, have been used for the preparation of some Co(III)-complexes with edda-type ligands [13, 15, 16–18]. When the ethylenediamine-N,N'-diacetate ion (edda) coordinates to Co(III) to form [Co(edda)(am)] (am: α-amino carboxylate ion), the edda prefers to take a symmetric coordination mode (*s-cis*) rather than an unsymmetric one (*uns-cis*) [3, 19, 20] in most synthetic routes [1–14]. It has been suggested that chelate strain of the carboxylate rings in *uns-cis*-edda complexes may be a contributing factor in determining the configuration of the edda ligand [13]. However, eddp, with longer carboxylate arms than edda and 1,3-pdda with a longer diamine moiety than edda, prefer unsymmetric modes [15, 16], suggesting that the size of the chelate ring has a profound effect on the distribution of geometrical isomers.

In this paper, *s-cis*-[Co(edda)(sar)], *mer-uns-cis*-[Co(edda)(sar)], *mer-uns-cis* [Co(eddp)(sar)] are reported. Also, the previously synthesized species *mer-uns-cis*-[Co(1,3-pddp)(sar)] [18] has been prepared by new route (direct

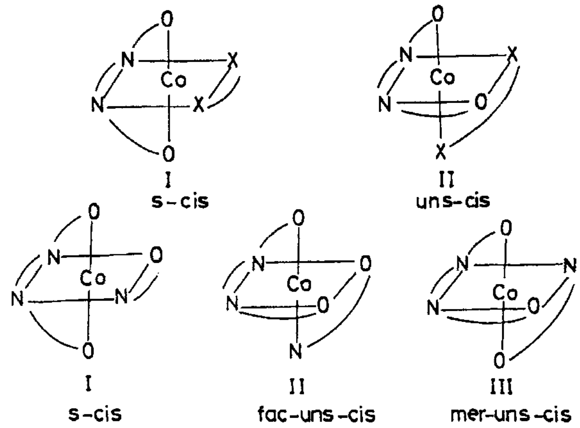

FIGURE 1 Possible geometrical isomers of [Co(eddp)L] complexes, (a) *s-cis*(I), *uns-cis*(II) for symmetrical bidentate ligands; (b) *s-cis*(I), *fac-uns-cis*(II) and *mer-uns-cis*(III), for unsymmetrical bidentate ligands.

reaction). The stereochemistry of the isolated complexes was investigated through ion-exchange chromatography, electronic absorption and infrared spectra and *H* nuclear magnetic resonance spectroscopy.

EXPERIMENTAL

Materials

Sodium *uns-cis*-(ethylenediamine-*N*, *N'*-di-3-propionato)(carbonato) cobaltate(III) and sodium ethylenediamine-*N*, *N'*diacetato(carbonato) cobaltate(III) were prepared using a previously described procedure [1, 14]. Other reagents were obtained commercially and used without further purification.

Meridional uns-cis-(ethylenediamine-N,N'-di-3-propionato)(sarcosinato) cobalt(III)monohydrate, [Co(eddp)(sar)]·H_2O

To a solution 1.00 g (2.6 mmol) of *uns-cis*-$Na[Co(eddp)CO_3]\cdot 2H_2O$ in 20.0 cm^3 of water, 0.463 g (5.2 mmol) of sarcosine in 10 cm^3 of water previously neutralized by 0.291 g (5.2 mmol) of KOH was added and the pH of the solution was adjusted to 8. After stirring and heating during 2 h at 75°C, the solution was evaporated to 10 cm^3 and introduced into a 2.5 × 32 cm column containing Sephadex G-10. The violet eluate was then poured into a 2 × 10 cm column containing Dowex 1-X4 (200–400 mesh) anion exchange resin in the Cl^- form. In both cases water was used as eluant.

The unreacted anionic complex was adsorbed on the top of the anion exchange resin while the neutral complex was eluted with water. One violet band appeared on the column. The eluate was evaporated to small volume and left in a refrigerator over night. The resulting crystals were filtered off, washed with ethanol, then ether and air dried. Yield: 0.43 g (44.1%) of the violet (*meridional*) isomer. *Anal.* Calcd. for *mer-uns-cis*-[Co(eddp) (sar)]·H_2O(%): C, 35.98; H, 6.04; N, 11.44. Found: C, 36.11; H, 6.52; N, 11.06.

Preparation of the Meridional Isomers s-cis- and uns-cis-(ethylenediamine-N,N'-diacetato)(sarcosinato)cobalt(III), [Co(edda)(sar)]

To a solution of 0.891 g (2.6 mmol) of $Na[Co(edda)CO_3]\cdot 1.5H_2O$ in 20.0 cm^3 of water 0.463 g (5.2 mmol) of sarcosine in 10 cm^3 of water previously neutralized by 0.291 g (5.2 mmol) of KOH was added and pH of the solution was adjusted to 8. After stirring and heating during 2 h at 75°C, the solution was evaporated to 10 cm^3 and chromatographed as described above.

The unreacted anionic complex was adsorbed on the top of the anion exchange resin. Three bands appeared on the column, purple (first), red-purple (second) and red (third). The red isomer was obtained as a minor product. The purple and red-purple eluates were evaporated to small volume and left in a refrigerator over night. The resulting crystals were filtered off, washed with ethanol, then ether and air dried. Yields: 0.084 g (9.8%) of purple (*s-cis*) and 0.057 g (6.5%) of red-purple (*mer-uns-cis*) isomers. *Anal.* Calcd. for *s-cis*-[Co(edda)(sar)]·$0.5H_2O$(%): C, 32.73; H, 5.15; N, 12.73. Found: C, 32.21; H, 5.36; N, 13.00. Calcd. for *mer-uns-cis*-[Co(edda)(sar)]·$2H_2O$: C, 30.26; H, 5.60; N, 11.76. Found: C, 30.73; H, 5.81; N, 11.60.

Preparation of Meridional uns-cis-(propylenediamine-N,N′-diacetato)(sarcosinato)cobalt(III)monohydrate, [Co(1,3-pdda)(sar)]·H_2O

A solution containing 2.63 g (0.01 mol) of 1,3-pdda·2HCl, 0.89 g (0.01 mol) of sarcosine, and 2.38 g (0.01 mol) of $CoCl_2 \cdot 6H_2O$ in 50.0 cm^3 of water was adjusted to pH 5 with a 1 M NaOH. The pH was kept constant at 5 and PbO_2 (7 g) was stirred into the solution at 40°C. After 1 h, insoluble materials were removed by filtration. The filtrate was poured into a SP-Sephadex column (10 × 25 cm, K^+ form) and eluted with water. Cationic complex was adsorbed on the column and neutral complex was eluated. The violet eluate containing neutral complex was poured into a 2.5 × 32 cm column containing Sephadex G-10. The column was washed with water to remove KCl and NaCl. The eluate was evaporated to small volume and left in a refrigerator over night. The resulting crystals were filtered off, washed with ethanol, than ether and air-dried. Yield: 0.13 g (3.8%) of violet (*meridional*) isomer. *Anal.* Calcd. for *mer-uns-cis*-[Co(1,3-pdda) (sar)]·$0.5H_2O$(%): C, 34.89; H, 5.57; N, 12.21. Found: C, 35.07; H, 5.44; N, 12.17.

Spectroscopic Measurements

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. For these measurements 1×10^{-3} mol dm^{-3} aqueous solutions of complexes were used. Proton NMR spectra was recorded on a Varian Gemini-200 NMR spectrometer using TMS as external reference in D_2O.

RESULTS AND DISCUSSION

Three geometrical isomers of (edda-type)Co(III)complexes with unsymmetrical bidentate ligands are theoretically possible, *s-cis*, *fac-uns-cis* and *mer-uns-cis* (Fig. 1). The edda-Co(III) and eddp-Co(III) complexes were prepared by displacement of carbonate ligand from the $[Co(edda)CO_3]^-$ and $[Co(eddp)CO_3]^-$ complexes.

The reaction of $Na[Co(edda)CO_3]$ and sarcosine produced a mixture of *s-cis* and *mer-uns-cis* isomers of [Co(edda)(sar)]. *Fac-uns-cis* isomer was also formed in this reaction as a minor product. The *s-cis* isomer is purple, the *mer-uns-cis* isomer is red-purple and the *fac-uns-cis* isomer is red. The order of column elution of the isomers is *s-cis*, *mer-uns-cis* and then *fac-uns-cis*.

However, since we used *uns-cis*-$Na[Co(eddp)CO_3]$ complex, [1] as the starting material for the preparation Na[Co(eddp)(sar)], substitution of CO_3^{2-} with sarcosine should theoretically give two geometrical isomers *fac-uns-cis* and *mer-uns-cis*, of [Co(eddp)(sar)] (Fig. 1). Only the *meridional* (violet) isomer *uns-cis*-[Co(eddp)(sar)] was obtained. By direct reaction of cobalt(II) chloride hexahydrate with sarcosine and 1,3-pdda in the present of lead(IV) oxide only *mer-uns-cis*-[Co(pdda)(sar)] was obtained. The fact that during these syntheses the *facial* isomers were not detected can be explained as being due to greater non-bonding interactions between edda-type ligands and the methyl group on sarcosine.

Electronic Absorption Spectra

Data concerning electronic absorption spectra of *mer* isomers of *s-cis*-[Co(edda)(sar)], *uns-cis*-[Co(edda)(sar)], *uns-cis*[Co(eddp)(sar)] and *uns-cis*-[Co(pddp)(sar)] are summarized in Table I. The two spin-allowed transitions in a low-spin d^6 system in an octahedral crystal field are $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ in order of increasing energy. In a tetragonal field, the degeneracies of the excited states are removed, *i.e.*, $^1T_{1g} = {}^1A_{2g} + {}^1E_g^a$ and $^1T_{2g} = {}^1B_{2g} + {}^1E_g^b$. With further decrease of molecular symmetry further splitting is expected. Small differences between states do not cause splitting of the absorption bands, especially of complexes with edda-type ligands and derivatives with lower symmetry than D_{4h} [21].

TABLE I Band Maxima in the visible spectra of some [Co(edda)*l*], [Co(1,3-pdda)*l*] and [Co(eddp)*l*] complexes

	I		II		
Complex	λ_1	ε_1	λ_2	ε_2	*Ref.*
s-cis-[Co(edda)CO_3]$^-$	565	114	382	128	14
uns-cis-[Co(edda)CO_3]$^-$	533	234	390	182	14
uns-cis-[Co(eddp)CO_3]$^-$	544	232	383	165	1
uns-cis-[Co(pdda)CO_3]$^-$	550	170	390	182	31
uns-cis-[Co(edda)gly]	542	116	372	133	30
fac-uns-cis-[Co(edda)gly]	520	223	374	–	30
mer-uns-cis-[Co(edda)gly]	525	94	370	128	30
fac-uns-cis-[Co(eddp)gly]	529	285	381	126	16
mer-uns-cis-[Co(eddp)gly]	564	97	381	123	16
s-cis-[Co(edda)sar]	540	101	374	133	this work
mer-uns-cis-[Co(edda)sar]	499	147	371	175	
	552	95			
mer-uns-cis-[Co(l, 3-pdda)sar]	530	107	378	162	
mer-uns-cis-[Co(eddp)sar]	499	173	375	160	
	566	113			

* Wavelength (λ) in nm. Extinction coefficient (ε) in M cm^{-1}, L = bidentate ligand.

The more symmetrical *facial* isomer has a cubic crystal field while the *meridional* isomer has a rhombic crystal field. This loss of symmetry has been observed previously in other CoN_3O_3 systems possessing *facial* and *meridional* isomers [22]. A definite shoulder is found for the low-energy absorption band of *meridional s-cis*-[Co(edda)(S-ala)] [4].

In previously reported papers [1 – 14] it has been shown that complexes with *s-cis* configuration of coordinated edda-type tetradentates have maxima of the first absorption bands at longer wavelengths than corresponding *uns-cis* isomers. The electronic absorption spectra of the investigated complexes show that the purple isomers have maxima of the first absorption bands at longer wavelengths than the red-purple isomers (Tab. I). These facts lead to the conclusion that the purple complex is the *s-cis* isomer while the red-purple complex is the *mer-uns-cis*-isomer. It has been noted also that Co(III) complexes with five-membered carboxylate chelate rings have first absorption bands at lower wavelengths than corresponding complexes with six-membered chelate rings [1, 23]. Our results confirm those facts.

Infrared Spectra

Important IR data for the *s-cis* and *uns-cis* isomers of the complexes are given in Table II. Asymmetric stretching frequencies of the carboxylate moieties were established as criteria for distinguishing between protonated

TABLE II Characteristic IR bands (cm^{-1}) for the complexes

Complex	ν (NH_2)	ν_{as} (COO^-)	ν_s (COO^-)
s-cis-[Co(edda)sar]	3442	1641	1359
mer-uns-cis-[Co(edda)sar]	3443	1641	1358
mer-uns-cis-[Co(eddp)sar]	3425	1598	1398

carboxylate groups (1700 – 1750 cm^{-1}) and coordinated carboxylate groups (1600 – 1650 cm^{-1}) [24]. All complexes showed a strong absorption around 1600 cm^{-1}, the CO-asymmetric stretching region. The lack of absorption between 1700 – 1750 cm^{-1} indicates that the carboxyl groups of tetradentate ligands are definitely coordinated to the central cobalt(III) ion. Also, it was demonstrated that the asymmetric stretching bands of the carboxylate groups of the five-membered chelate rings lie at higher energy than the corresponding bands of the six-membered chelate rings [23, 25 – 29]. 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.

Proton NMR Spectra

^1H NMR spectra has been used widely in characterization of metal chelates containing aminocarboxylate ligands [7, 14, 16, 32]. ^1H NMR spectra of the isolated complexes are shown in Figure 2. In the *s-cis* isomer of the [Co(edda)(sar)] the two glycinate rings of edda are equivalent and only one AB quartet due to the glycinate ring protons can be expected at δ 4.1 to 4.4. The *uns-cis* isomer exhibits a more complex spectrum in the glycinate region where an intense peak is observed at δ 3.7 superimposed on the same type of AB quartet (δ 3.6 to 4.1) found in the *s-cis* isomers. Protons associated with the N—CH_2—CH_2—N ring are found at δ 3.1 to 3.6 and at δ 3.0 to 3.4 for *s-cis* and *uns-cis* isomers, respectively. The methyl resonance of sarcosine is at δ 2.7 for the *s-cis* isomer and δ 2.6 for the *uns-cis* isomer.

The NMR spectrum of the *mer-uns-cis*-[Co(eddp)sar] appears to be more complex than those observed for the edda-Co(III) complex. Because of its highly collapsed nature and overlap of signals, a complete analysis is difficult. The protons associated with the both β-alaninato rings (from eddp) and the glycinato ring (from sar) are in the region δ 3.5 to 3.9. Protons associated with the N—CH_2—CH_2—N ring of eddp are found between δ 2.9 and 3.2. The methyl resonance of the sarcosine is centered at δ 2.8. The appearance of the multiplet can be attributed to spin – spin coupling

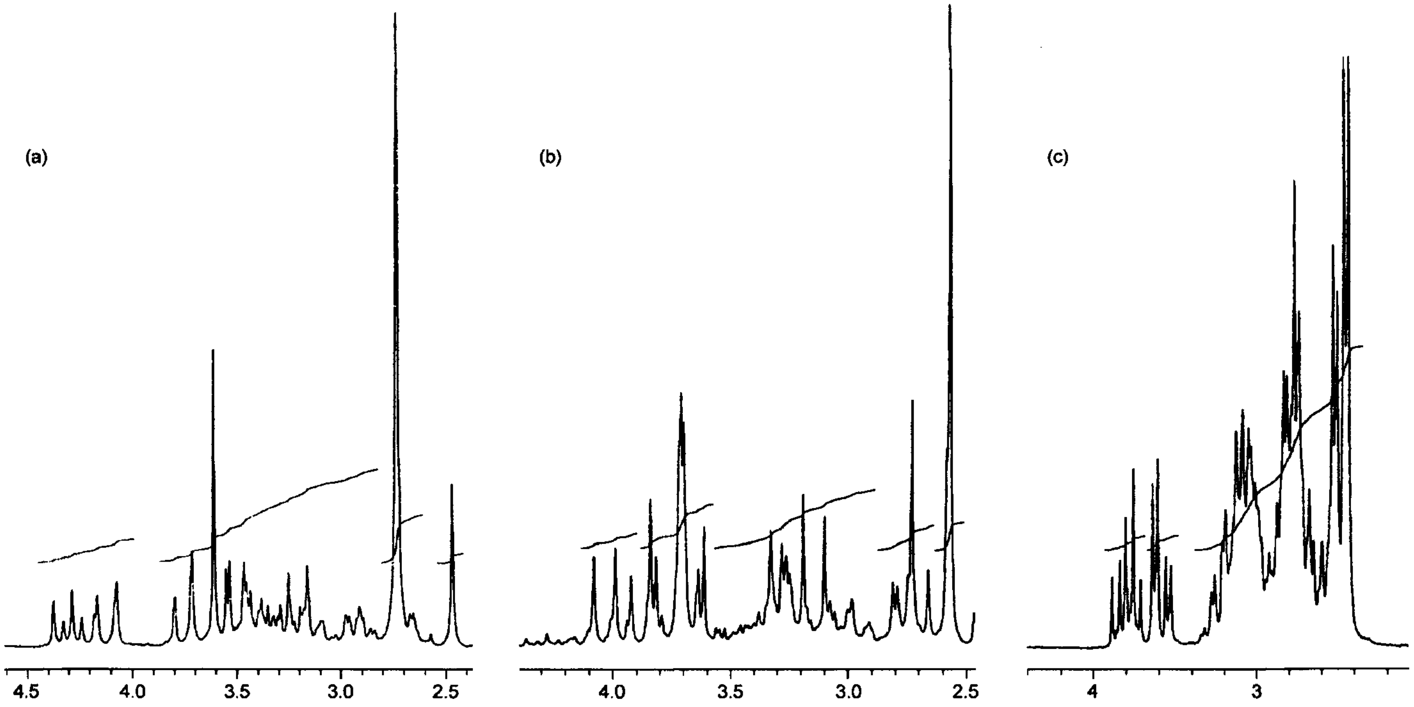

FIGURE 2 ^{1}H NMR spectra of (a) *s-cis*-[Co(edda)sar], (b) *mer-uns-cis*-[Co(edda)sar] and (c) *mer-uns-cis*-[Co(eddp)sar].

with the amino protons which had not completely changed with deuterium at the time of measurement.

Acknowledgements

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

References

[1] D. J. Radanović, M. I. Djuran, V. D. Miletić and R. R. Parijez, *J. Serb. Chem. Soc.* **50**, 99 (1985).
[2] M. Mori, M. Shibata, E. Kyuno and F. Maruyama, *Bull. Chem. Soc. Jpn.* **35**, 75 (1962).
[3] J. I. Legg and D. W. Cooke, *Inorg. Chem.* **4**, 1576 (1965).
[4] J. I. Legg, D. W. Cooke and B. E. Douglas, *Ibid.* **6**, 700 (1967).
[5] J. I. Legg and B. E. Douglas, *Ibid.* **7**, 1452 (1968).
[6] C. W. Van Saun and B. E. Douglas, *Ibid.* **8**, 115 (1969).
[7] P. F. Coleman, J. I. Legg and J. Steele, *Ibid.* **9**, 937 (1970).
[8] K. Kuroda and K. Watanabe, *Bull. Chem. Soc. Jpn.* **44**, 1034 (1971).
[9] K. Kuroda, *Ibid.* **45**, 2176 (1972).
[10] W. T. Jordan and B. E. Douglas, *Inorg. Chem.* **12**, 403 (1973).
[11] K. Kuroda, *Chem. Lett.* **1**, 17 (1974).
[12] W. T. Jordan and J. I. Legg, *Inorg. Chem.* **13**, 955 (1974).
[13] L. J. Halloran and J. I. Legg, *Ibid.* **13**, 2193 (1974).
[14] P. J. Gannett and D. W. Watts, *Inorg. Chim. Acta* **8**, 293 (1974).
[15] M. Okabayashi, K. Igi and J. Hidaka, *Bull. Chem. Soc. Jpn.* **52**, 753 (1979).
[16] T. J. Sabo, S. R. Grgurić, D. M. Minić and S. R. Trifunović, *J. Coord. Chem.* **44**, 47 (1998).
[17] K. Akamatsu, T. Komorita and Y. Shimura, *Bull. Chem. Soc. Jpn.* **55**, 2390 (1982).
[18] M. Okabayashi, K. Okamoto and J. Hidaka, *Bull. Chem. Soc. Jpn.* **53**, 2257 (1980).
[19] W. E. Keyes and J. I. Legg, *J. Am. Chem. Soc.* **98**, 4970 (1976).
[20] L. J. Halloran and J. I. Legg, *Inorg. Chem.* **9**, 2193 (1974).
[21] F. Basolo, C. J. Ballhausen and J. Bjerrum, *Acta Chem. Scand.* **9**, 810 (1955); Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Jpn.* **29**, 311 (1956).
[22] Y. Shimura, *Bull. Chem. Soc. Jpn.* **31**, 173 (1958); B. E. Douglas and S. Yamada, *Inorg. Chem.* **4**, 1561 (1965); J. H. Dunlop and R. D. Gillard, *J. Chem. Soc.* 6531 (1965).
[23] M. B. Ćelap, S. R. Niketić, T. J. Janjić and V. N. Nikolić, *Inorg. Chem.* **6**, 2063 (1967).
[24] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds". (John Wiley and Sons, New York, 1963).
[25] D. H. Busch and J. C. Bailar Jr., *J. Am. Chem. Soc.* **75**, 4574 (1953); **78**, 716 (1956).
[26] M. L. Morris and D. H. Busch, *Ibid.* **78**, 5178 (1956).
[27] J. A. Neal and N. J. Rose, *Inorg. Chem.* **7**, 2405 (1968); **12**, 1226 (1973).
[28] J. A. Broomhead, M. Dwyer and N. Kane-Maguire, *Ibid.* **7**, 1388 (1968).
[29] D. J. Radanović and B. E. Douglas, *J. Coord. Chem.* **4**,191 (1975).
[30] H. Nakazawa, H. Ohtsuru and H. Yoneda, *Bull. Chem. Soc. Jpn.* **60**, 525 (1987).
[31] K. Igi and B. E. Douglas, *Inorg. Chim. Acta* **10**, 109 (1974).
[32] J. L. Sudmeier and G. Occupati, *Inorg. Chem.* **7**, 2524 (1968).