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Characterization studies and cyclic voltammetry on nickel(II) amino acid dithiocarbamates with triphenylphosphine in the coordination sphere

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Abstract: Nickel(II) amino acid dithiocarbamate complexes of the composition $[Ni(AAdtc)(PPh_3)(NCS)]$, $[Ni(AAdtc)(PPh_3)(CN)]$ and $[Ni(AAdtc)(PPh_3)_2]ClO_4$ [(AAdtc = dithiocarbamate derivatives of amino acids, *i.e.*, glycine (glydtc), L-*iso*-leucine (*i*-leudtc) and L-proline (prodtc)] were synthesized. The compounds were characterized by IR and electronic spectroscopy, thermal analysis, cyclic voltammetry and conductivity measurements. In the case of the mixed ligand complexes, the thioureide ν(C–N) values were shifted to higher wave numbers compared to $[Ni(AAdtc)_2]$. This observation shows the increased strength of the thioureide bond due to the presence of the π-accepting phosphine. Electronic spectral studies suggest square planar geometry for the complexes. Thermal analyses of the complexes are in keeping with the proposed formulae. Almost all the complexes showed signs of decay above 170 °C. At around 390 °C, the final mass corresponded to NiS. Cyclic voltammetry showed a decrease of the electron density on the nickel in the mixed ligand complexes compared to $[Ni(AAdtc)_2]$.

Keywords: amino acid dithiocarbamate; triphenylphosphine; nickel(II); IR; electronic spectra; cyclic voltammetry.

INTRODUCTION

Group VIII dithiolates containing planar MS_4 chromophores show interesting variations in their reactions with Lewis bases.[1,2] Unlike its congeners, nickel(II) is a borderline acceptor and its planar dithiocarbamate ligand prefers to react with Lewis bases, such as phosphines, rather than hard nitrogenous bases. Nickel(II) dithiocarbamates in their reaction with PR_3 form NiS_2P_2 chromophores.[3,4]

Nickel(II) complexes with phosphine ligands have been studied for their anti-cancer activity.[5] Many proteins contain cystein and methionine residues and hence dithiocarbamate derivatives of α-amino acids may be valid models for the study of the coordination of proteins to metal ions. The complexes formed between metal

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ions and dithiocarbamate derivatives of amino acids have been reported.[6–8] In order to understand the influence of SCN^- and CN^- donors on the coordination environment around a nickel atom and on the thioureide bond, in this work, the synthesis and characterization of mixed-ligand complexes *i.e.*, $[Ni(AAdtc)(PPh_3)(NCS)]$, $[Ni(AAdtc)(PPh_3)(CN)]$ and $[Ni(AAdtc)(PPh_3)_2]ClO_4$, were studied.

EXPERIMENTAL

Synthesis of the ligands

The dithiocarbamate-derivatives of the α-amino acids glycine, L-*iso*-leucine and L-proline were synthesized following a method similar to that described by Musil and Irgolic.[9] The amino acid (0.050 mol) was reacted with an aqueous solution of $Ba(OH)_2 \cdot 8H_2O$ (0.055 mol) and the suspension was magnetically stirred until total dissolution was achieved. In order to prevent precipitation of barium carbonate, the presence of air was avoided. Acetone was then added, until its content was *ca.* 40 % of the total volume and CS_2 (0.060 mol) was added dropwise. Formation of the barium salt occurs according to the reaction:

$$H_2N{-}CH(R){-}COOH + Ba(OH)_2 + CS_2 \rightarrow Ba(S_2C{-}NH{-}CH(R){-}COO) + 2H_2O$$

The solution was kept at 0 °C for 12 h. Addition of ethanol resulted in a white precipitate, which was filtered and washed with diethyl ether. Purification was performed by dissolution in water and precipitation with ethanol.

Preparation of nickel(II)-dithiocarbamate complexes

A solution of $NiCl_2 \cdot 6H_2O$ (0.001 mol) was added dropwise to an aqueous solution of the barium salt (0.001 mol) of the corresponding dithiocarbamate ligand. The light green nickel(II) solution immediately became dark and a precipitate formed, which was characterized as $Ba[Ni(S_2C{-}NH{-}CH(R){-}COO)_2] \cdot 3H_2O$. In order to remove the barium cation from the complex, the aqueous solution was transferred to a separating funnel and diethyl ether was added. Then the stoichiometric amount of 0.10 M HCl was added to generate $BaCl_2$, which remained in the aqueous layer. It should be noted that the acid solution was added after the diethyl ether, hence, the neutral complex was removed to the organic phase before it was destroyed by the acidic medium:

$$2Ba(S_2C{-}NH{-}CH(R){-}COO) + NiCl_2 + 2HCl \rightarrow Ni(S_2C{-}NH{-}CH(R){-}COOH)_2 + 2BaCl_2$$

Upon evaporation of the diethyl ether, the olive green $Ni(AAdtc)_2$ complex separated.

*Preparation of [Ni(AAdtc)(PPh$_3$)(NCS)] [AAdtc = glydtc (**1**), i-leudtc (**2**), prodtc (**3**)]*

A mixture of $Ni(AAdtc)_2$ (0.001 mol), $NiCl_2 \cdot 6H_2O$ (0.001 mol), PPh_3 (0.002 mol) and NH_4SCN (0.002 mol) was refluxed for 3 h in acetonitrile (30 cm^3) and methanol (10 cm^3). The purple red solution was filtered and left to evaporate. After two days, a purple red solid had separated out, which was re-crystallized from $CHCl_3$.

*Preparation of [Ni(AAdtc)(PPh$_3$)(CN)] [AAdtc = glydtc (**4**), i-leudtc (**5**), prodtc (**6**)]*

A mixture of $Ni(AAdtc)_2$ (0.001 mol), $NiCl_2 \cdot 6H_2O$ (0.001 mol), PPh_3 (0.002 mol) and KCN (0.002 mol) was refluxed for 3 h in acetonitrile (30 cm^3) and methanol (10 cm^3). The orange solution was filtered and left to evaporate. After two days, an orange solid separated out, which was recrystallized from Me_2CO.

*Preparation of [Ni(AAdtc)(PPh$_3$)$_2$]ClO$_4$ [AAdtc = glydtc (**7**), i-leudtc (**8**), prodtc (**9**)]*

A mixture of $Ni(AAdtc)_2$ (0.001 mol), $NiCl_2 \cdot 6H_2O$ (0.001 mol), PPh_3 (0.002 mol) and $NaClO_4$ (0.001 mol) in $CHCl_3$ (50 cm^3) and EtOH (4 cm^3) was refluxed for 3 h. The resulting purple red solution was filtered and left to evaporate. After 2 days, a purple red solid separated, which was recrystallized from $CHCl_3$.[10]

Analytical and physical measurements

Reagent grade, high purity materials (BDH/Merck) were used as supplied. The nitrogen content in the complex was determined by the Kjeldahl method and the nickel content was determined by the standard EDTA method. The conductivity studies were performed using a Pico Model 201 conductivity bridge. Acetone and acetonitrile were used as solvents. The conductance measurements were recorded at room temperature (27 °C). The concentration of the compounds was 1×10^{-3} mol dm^{-3} in all measurements. IR Spectra were recorded as KBr pellets with a Nicolet Avatar 360 FT-IR spectrophotometer (range 400–4000 cm^{-1}). UV–Vis spectra were recorded on a Hitachi U-2001 double beam UV-spectrophotometer. A Perkin–Elmer TGA7 instrument was used for the thermal analysis. The heating rate of the furnace was fixed at 20 °C min^{-1}. An ECDA 001 electrochemical system was used for recording the cyclic voltammograms of the complexes. The working electrode was made of glassy carbon. The counter electrode was a Pt wire and reference electrode was Ag/AgCl. Pure dichloromethane was used as the solvent and tetrabutylammonium perchlorate (0.10 M) as the supporting electrolyte. The scan rate employed was 100 mV s^{-1}. All measurements were recorded at room temperature (27 °C) in an oxygen free atmosphere, provided by bubbling purified nitrogen through the solution. The concentration of the compounds was 1×10^{-3} mol dm^{-3}.

RESULTS AND DISCUSSION

The conductivity measurements indicated the non-electrolytic nature of the complexes **1–3** and **4–6** and the 1:1 electrolytic nature of the complexes **7–9**,[11] Table I.

Infrared spectra

The important IR bands are listed in Table I. The energy of the ν(C−N) band was intermediate between the stretching frequencies associated with typical single and double bonded carbon and nitrogen atoms.[12] The Ni(AAdtc)$_2$ complexes showed the thioureide stretching bands at *ca.* 1500 cm^{-1}. In the case of the mixed ligand complexes, the ν(C−N) values were found to be larger than those of the parent dithiocarbamates. This observation shows the increased strength of the thioureide bond due to the presence of the π-accepting phosphine. In general, the glydtc and *i*-leudtc complexes showed higher thioureide ν(C−N) values than the prodtc complexes because the heterocyclic ring system has a smaller tendency to release electrons to the N−C bond.[13]

The ν(C−N) bands (single bonded) appeared at *ca.* 1100 cm^{-1}**,** while in the mixed ligand complexes containing the perchlorate anion, a band due to ClO_4^- ions also appeared in this region. The IR spectral bands at 2090 cm^{-1} ν(C≡N) and 830 cm^{-1} ν(C−S) for the complexes **1–3** may imply the assumption that the NCS group is coordinated to the nickel *via* the nitrogen atom.[14] In the case of complexes **4–6**, the ν(C≡N) frequency at *ca.* 2135 cm^{-1} indicates the CN$^-$ group is bonded to the metal through the carbon atom.[15]

The ν(C−S) asymmetric stretching bands are located prominently at *ca.* 1000 cm^{-1} in all the complexes and the ν(C–S) symmetric bands appear as weak absorptions at *ca*. 690 cm^{-1}. All the complexes show bands at 1700±30 cm^{-1}, indicating the presence of free carboxylic groups.[16] This observation shows that the carboxylic group is not involved in the coordination.

TABLE I. Important IR bands, conductance and analytical data for the complexes

Compound	Important infrared spectral bands cm^{-1}				λ_m S cm^2 mol^{-1}	Found (Calcd.) %	
	ν(C–N) (Thioureide)	ν(C–N) (Single bonded)	ν(C–N) (NCS/CN)	ν(C–S)		Ni	N
[Ni(glydtc)(PPh$_3$)(NCS)] (**1**)	1542	1098	2094	1017	11.78[a]	11.0 (11.2)	5.2 (5.3)
[Ni(i-leudtc)(PPh$_3$)(NCS)] (**2**)	1520	1098	2091	1030	10.04[a]	9.8 (10.1)	4.6 (4.8)
[Ni(prodtc)(PPh$_3$)(NCS)] (**3**)	1510	1099	2088	1034	8.01[a]	10.3 (10.4)	4.6 (4.9)
[Ni(glydtc)(PPh$_3$)(CN)] (**4**)	1536	1098	2137	1028	14.56[b]	11.5 (11.9)	5.4 (5.6)
[Ni(^{i}leudtc)(PPh$_3$)(CN)] (**5**)	1540	1097	2137	1026	15.30[b]	10.6 (10.7)	4.8 (5.1)
[Ni(prodtc)(PPh$_3$)(CN)] (**6**)	1511	1097	2132	1028	9.88[b]	10.8 (11.0)	4.9 (5.2)
[Ni(glydtc)(PPh$_3$)$_2$]ClO$_4$ (**7**)	1539	1115	–	1028	121.76[a]	6.8 (7.1)	1.3 (1.7)
[Ni(^{i}leudtc)(PPh$_3$)$_2$]ClO$_4$ (**8**)	1529	1099	–	1028	118.46[a]	6.6 (6.7)	1.4 (1.6)
[Ni(prodtc)(PPh$_3$)$_2$]ClO$_4$ (**9**)	1512	1090	–	1028	138.80[a]	6.5 (6.8)	1.2 (1.6)

[a]Measured in acetone solution, [Ni^{+2}] = 10^{-3} mol dm^{-3} at 27 °C; [b]measured in acetonitrile solution, [Ni^{+2}] = = 10^{-3} mol dm^{-3} at 27 °C

Electronic spectra

In all the nickel(II) complexes, the bands which appear below 350 nm are due to intraligand π–π* transitions, mainly associated with N−C=S and S−C=S groups (Table II). Several authors ascribe the intense bands at 390 nm to either metal → ligand or ligand → metal charge transfer.[17] In addition to these charge transfer bands, the electronic spectra show weak bands at 490 and 650 nm, due to the d–d transitions. In the dialkyldithiocarbamato complexes of nickel(II), similar bands were reported and ascribed to transitions from the lower filled d-orbitals to the unoccupied $d_{x^2-y^2}$ orbitals.[18] The two bands at 650 and 490 nm correspond to $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{z^2} \rightarrow d_{x^2-y^2}$ transitions, respectively.

The strong bands at around 490, 435 and 440 nm for the complexes **1**–**9** can be attributed to d–d electron transitions, Table I. Comparison of the information already available on similar compounds of this type leads to the conclusion that the coordination around the metal ions should be square planar.[3,4]

TABLE II. Electronic spectral bands, thermogravimetric data and cyclic voltammetric reduction potentials

Compound	λ_{max} / nm	Decomp. temp. °C	Weight loss, %		Final residue	Reduction potential, V
			Exp.	Calcd.		
[Ni(glydtc)(PPh$_3$)(NCS)] (**1**)	332, 385, 485	182–382	83.4	82.8	NiS	–0.816
[Ni(i-leudtc)(PPh$_3$)(NCS)] (**2**)	258, 329, 490	180–368	82.7	84.5	NiS	–0.837
[Ni(prodtc)(PPh$_3$)(NCS)] (**3**)	252, 329, 491	192–377	84.0	84.1	NiS	–0.841
[Ni(glydtc)(PPh$_3$)(CN)] (**4**)	218, 254, 321, 432	167–394	80.7	81.7	NiS	–1.092
[Ni(^{i}leudtc)(PPh$_3$)(CN)] (**5**)	241, 309, 438	190–370	82.7	83.6	NiS	–1.001
[Ni(prodtc)(PPh$_3$)(CN)] (**6**)	225, 309, 433	177–376	82.0	83.3	NiS	–1.010
[Ni(glydtc)(PPh$_3$)$_2$]ClO$_4$ (**7**)[a]	239, 258, 324, 440	–	–	–	–	–0.645
[Ni(^{i}leudtc)(PPh$_3$)$_2$]ClO$_4$ (**8**)[a]	256, 325, 440	–	–	–	–	–0.652
[Ni(prodtc)(PPh$_3$)$_2$]ClO$_4$ (**9**)[a]	256, 327, 440	–	–	–	–	–0.617

[a] The decomposition of the complexes containing the perchlorate anion were not performed owing to their possible explosive character

Thermal analysis

TG Techniques were employed to follow the thermal behavior of complexes **1**–**6**. Representative thermograms of [Ni(glydtc)(PPh$_3$)(NCS)] and [Ni(*i*-leudtc)(PPh$_3$)(NCS)] are given in Fig. 1. According to the results obtained, the

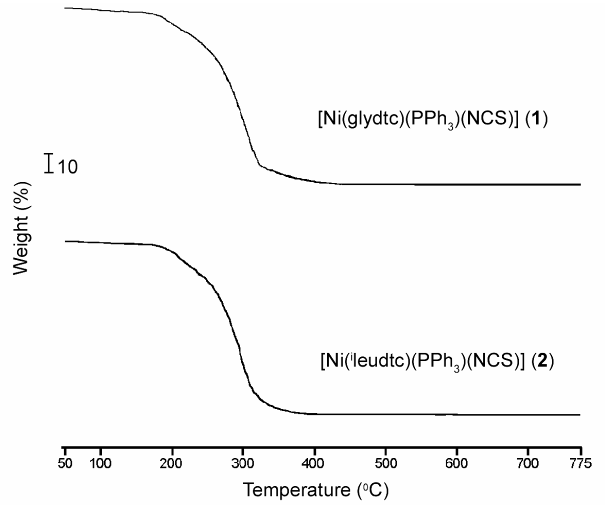


Fig. 1. Thermograms of [Ni(glydtc)(PPh$_3$)(NCS)] (**1**) and [Ni(*i*-leudtc)(PPh$_3$)(NCS)] (**2**).

complexes are not volatile and their decomposition occurs in different steps; the main features are summarized in Table I. Thermogravimetric studies on the complexes confirmed their proposed molecular formulae. The thermograms of all the complexes show an initial decomposition around 180 °C, which indicates the absence of solvent molecules. Complexes **1**, **3**, **6** and **9** show similar behavior with three main processes. The other complexes show two main processes, probably corresponding to pyrolysis of the organic matter existing in these compounds. The final product of the decomposition is nickel sulfide, as confirmed by the experimental and expected weight loss measurements.

Cyclic voltammetry

The cyclic voltammetry reduction potentials are given in Table II. Representative cyclic voltammograms of [Ni(prodtc)$_2$] and [Ni(prodtc)(PPh$_3$)(NCS)] are given in Fig. 2. The reduction potential for the parent Ni(AAdtc)$_2$ complexes is observed around −1.3 V. All the mixed-ligand complexes **1**–**9** show one electron

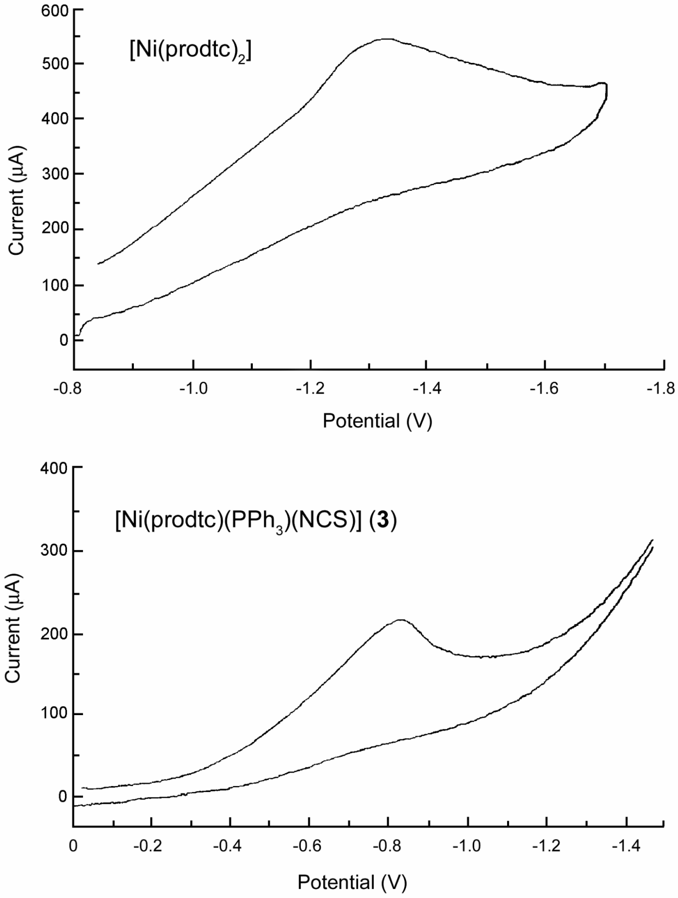
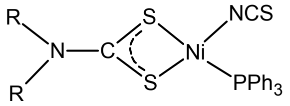


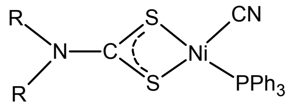
Fig. 2. Cyclic voltammograms of [Ni(prodtc)$_2$] and [Ni(prodtc)(PPh$_3$)(NCS)] (**3**).

reduction at lower potentials. The reductions are irreversible. The lower reduction potentials observed for complexes **1**–**9** indicate the ease of electron addition in the mixed-ligand complexes. The mesomeric drift of the electron density from the dithiocarbamate moiety towards the metal centre contributes to lower reduction potential from the normal reduction potentials of $Ni(dtc)_2$ complexes around –1.3 V.[19] Comparison of $[Ni(AAdtc)(PPh_3)_2]ClO_4$ with the other types of complexes show that the reduction potentials decrease in the following order: $Ni(AAdtc)_2$ > $[Ni(AAdtc)(PPh_3)(CN)]$ (**4**–**6**) > $[Ni(AAdtc)(PPh_3)(NCS)]$ (**1**–**3**) > > $[Ni(AAdtc)(PPh_3)_2]ClO_4$ (**7**–**9**), indicating the influence of the PPh_3, NCS and CN ligands, respectively, on the mesomeric drift of the electron density towards nickel.

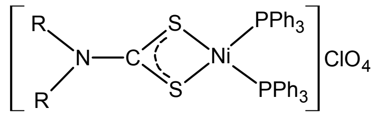
Infrared spectral studies on the complexes show the contribution of the thioureide form to the structures. In the case of mixed-ligand complexes, the ν(C−N) (thioureide) values shift to higher wave numbers compared to the $Ni(AAdtc)_2$ complexes. This observation is an indication of the increased electron density on nickel in the mixed ligand complexes and, hence, these complexes are expected



$[Ni(AAdtc)(PPh_3)(NCS)]$



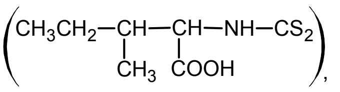
$[Ni(AAdtc)(PPh_3)(CN)]$



$[Ni(AAdtc)(PPh_3)_2]ClO_4$

R_2NCS_2 = AAdtc = glydtc ($HOOC\text{-}CH_2\text{-}NH\text{-}CS_2$),

ileudtc



$$\left(CH_3CH_2-\underset{CH_3}{CH}-\underset{COOH}{CH}-NH-CS_2\right),$$

Prodtc

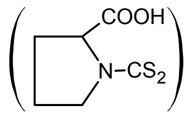


Fig. 3. Proposed structures of the complexes.

to be more difficult to reduce. However, in reality, the mixed-ligand complexes are the most easily reduced. The reason probably is extensive π-back bonding with the phosphorous atom, which drains the excess negative charge on the metal and hence the low reduction potential.

Based on the above observations, the structures proposed for these complexes are given in Fig. 3.

ИЗВОД

КАРАКТЕРИЗАЦИЈА И ЦИКЛИЧНА ВОЛТАМЕТРИЈА НИКАЛ(II) АМИНОКИСЕЛИНСКИХ ДИТИОКАРБАМАТА СА ТРИФЕНИЛФОСФИНОМ У КООРДИНАЦИОНОЈ СФЕРИ

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Синтетисани су комплекси никла(II) са аминокиселинским дитиокарбаматима састава: [Ni(AAdtc)(PPh$_3$)(NCS)], [Ni(AAdtc)(PPh$_3$)(CN)] и [Ni(AAdtc)(PPh$_3$)$_2$]ClO$_4$ [(AAdtc = дитиокарбаматни деривати аминокиселина, тј. глицина (glydtc), L-изолеуцина (*i*-leudtc) и L-пролина (prodtc)]. Једињења су окарактерисана IR и електронском спектроскопијом, термичком анализом, цикличном волтаметријом и мерењима проводљивости. У случају комплекса са мешовитим лигандима, тиоуреидне ν(C−N) вредности померају се ка већим таласним бројевима у поређењу са [Ni(AAdtc)$_2$]. Ово указује на јачу тиоуреидну везу због присуства π-акцепторског фосфина. Електронска спектрална проучавања указују на квадратно-планарну геометрију ових комплекса. Скоро сви комплекси показују знаке распада изнад 170 °C. На око 390 °C коначна маса одговарала је NiS. Циклична волтаметрија комплекса указује на смањење електронске густине на никлу у мешовито-лигандним комплексима у поређењу са [Ni(AAdtc)$_2$].

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REFERENCES

1. A. Chakravarthy, *Prog. Inorg. Chem.* **7** (1966) 83
2. J. P. Fackler Jr., W. C. Siegel, *Inorg. Chem.* **8** (1969) 163
3. C. K. Jorgenson, *Inorg. Chem.* **3** (1964) 120
4. R. Pastroek, J. Kamenicek, J. Marek, D. Dastych, Z. Sindelar, *Polyhedron* **19** (2000) 1713
5. P. S. Jarret, O. M. N. Dhubhghaill, P. J. Sadler, *J. Chem. Soc. Dalton Trans.* (1993) 1863
6. B. Macias, P. Malet, R. Paradinas, V. Rives, M. V. Villa, *Inorg. Chim. Acta* **127** (1999) 288
7. S. Thirumaran, K. Ramalingam, *Trans. Metal Chem.* **25** (2000) 60
8. I. R. Baird, B. R. Camneron, R. T. Skerlj, *Inorg. Chim. Acta* **353** (2003) 107
9. A. Musil, K. Irgolic, *Z. Anal. Chem.* **208** (1965) 352
10. W. J. Geary, *Coord. Chem. Rev.* **7 (**1971) 81
11. R. Baggio, A. Frigerio, E. B. Halac, D. Vega, M. Perec, *J. Chem. Soc. Dalton Trans.* (1992) 549
12. C. Moncotrigiano, G. C. Pellacani, C. Preti, *J. Inorg. Nucl. Chem.* **36** (1974) 3709
13. R. Pastorek, Z. Travenicek, E. Kvapilova, Z. Sindelar, F. Brezina, J. Marek, *Polyhedron* **18** (1999) 151
14. B. Arul Prakasam, K. Ramalingam, G. Bocelli, R. Olla, *Z. Anorg. Allg. Chem.* **630** (2004) 301
15. M. Castillo, M. J. Criado, B. Macias, V. Vaquero, *Inorg. Chim. Acta* **124** (1986) 127

16. W. Beck, M. Givnth, M. Castillo, H. Zippel, *Chem. Ber*. **11** (1978) 1246
17. C. K. Jorgenson, *J. Inorg. Nucl. Chem*. **24** (1962) 1571
18. K. Ramalingam, G. Aravamudan, M. Seshasayee, *Inorg. Chim. Acta* 128 (1987) 231.