

Transition Metal Promoted Addition of Methanol to Cyanoguanidine. Molecular Structure and Properties of the Generated Copper(II) and Nickel(II) Complexes

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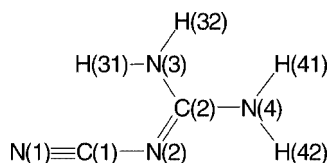
Abstract. The reaction of the Cu^{II} and Ni^{II} complexes of saccharin with dicyandiamide (cyanoguanidine, cnge) in methanol produces the addition of methanol to the nitrile moiety of this molecule. Furthermore, the product of the reaction coordinates the metal centers generating two new complexes containing saccharinate as the counter anion. The crystal structures of [Cu(cnge-OCH₃)₂](sac)₂ and of [Ni(cnge-OCH₃)₂](sac)₂·2H₂O (cnge-OCH₃ = 1-amidino-O-methylurea) were solved by single crystal X-ray diffractome-

try. Both complexes crystallize in the triclinic space group P $\bar{1}$ and the metallic cations present a quite similar centrosymmetric planar conformation. The complexes were characterized by means of electronic and infrared spectroscopy and also their magnetic and thermal behavior was investigated.

Keywords: Copper; Nickel; Saccharinate complexes; Methanol addition

1 Introduction

Cyanamide is a recognized substrate of nitrogenase [1]. Its dimer, dicyandiamide or cyanoguanidine (scheme 1) presents two tautomeric forms: N≡C-N=C(NH₂)₂ and N≡C-NHC(=NH)NH₂. This polyfunctional species has commercial and biological significance as a precursor for the synthesis of some organonitrogen compounds [2].

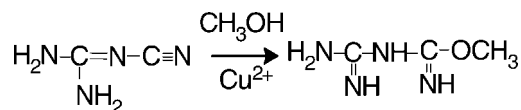


Scheme 1

Cyanoguanidine readily coordinates transition metal complexes. Coordination occurs through the nitrile nitrogen atom N(1). When the nitrile function is used in coordination, additional coordination through the N(2) atom is possible [3–8].

Transition-metal promoted reactions of cyanoguanidine, such as addition of water, alcohols and amines to generate the guanlylurea, 1-amidino-O-alkylureas, and biguanides, respectively, are well-known reactions [2, 9–13]. In particular, the reaction between methanol and cyanoguanidine (see scheme 2), does not occur in absence of Cu^{II} or Ni^{II}, even

at drastic experimental conditions. Moreover, other studies suggested that coordination of vinyl nitriles to Ni(II) centers activates its C=C bond toward 1,4-addition of amines [14].



Scheme 2

Furthermore, it is well known that saccharin (Hsac, o-sulphobenzimide) is a very versatile ligand which is able to produce a variety of mixed-ligand complexes, sharing the coordination sphere of metal centers with other ligands, or acting as a counteranion (for a recent review cf. [15]). As we have recently prepared a number of mixed-ligand complexes of this type, containing the saccharinate anion together with a second ligand in the coordination spheres of Zn^{II} [16, 17], Ni^{II} [18] and Cu^{II} [19, 20], we have now attempted to prepare similar complexes with saccharin and cyanoguanidine. Notwithstanding, under the employed experimental conditions, the starting copper and nickel bis(saccharinato)tetraaqua complexes produce the addition of the employed solvent (methanol) to cyanoguanidine generating two new cationic complexes containing 1-amidino-O-methylurea as ligand, in which saccharinate acts simply as counteranion.

2 Results and Discussion

2.1 Structural analysis

Crystal parameters and details of the used refinement procedure are given in Table 1 whereas the ORTEP [21] draw-

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Table 1 Crystal refinement data for the [Cu(cnge-OCH₃)₂](sac)₂ (1) and [Ni(cnge-OCH₃)₂](sac)₂·2H₂O (2) complexes

	(1)	(2)
Empirical formula	C ₂₀ H ₂₄ N ₁₀ O ₈ S ₂ Cu	C ₂₀ H ₂₈ N ₁₀ O ₁₀ S ₂ Ni
Formula weight	660.15	691.35
Crystal dimension/mm	0.16 x 0.14 x 0.03	0.14 x 0.10 x 0.04
Crystal system	triclinic	triclinic
Space group	P $\bar{1}$	P $\bar{1}$
<i>a</i> /Å	8.504(1)	7.448(1)
<i>b</i> /Å	9.127(1)	8.735(1)
<i>c</i> /Å	9.960(1)	11.359(1)
α /°	115.21(1)	71.06(1)
β /°	106.79(1)	88.24(1)
γ /°	93.28(1)	77.67(1)
Volume/Å ³	654.96(3)	682.2(1)
Z	1	1
D _{calc} /g·cm ⁻³	1.674	1.683
F(000)	339	358
θ -range for data collect.	2.84 – 27.48	2.52 – 24.99°
Nr. of reflections (total)	9927	10769
Independent reflections	2993 [R(int) = 0.0446]	2404 [R(int) = 0.0736]
Observed reflect.[I>2 σ (I)]	2499	2016
Data/restraints/parameters	2993/0/189	2404/0/217
Goodness-of-fit on F ²	1.033	1.047
Final R indices [I>2 σ (I)]	R1 = 0.0400 wR2 = 0.1087	R1 = 0.0432 wR2 = 0.1056
R indices (all data)	R1 = 0.0509 wR2 = 0.1184	R1 = 0.0546 wR2 = 0.1134
Larg. peak and hole/e.Å ⁻³	0.288 and -0.343	0.481 and -0.655

ings of the complexes are shown in Figures 1 and 2. The metal ion in both complexes is at a crystallographic inversion center in a square-planar environment, *cis*-coordinated to a pair of symmetry related 1-amidino-O-methylurea molecules acting as bidentate ligands through their terminal N-atoms. The M-N distances are 1.930(2) and 1.980(2) Å in the Cu(II) complex and 1.846(3) and 1.876(3) Å in the Ni^{II} complex. The “bite” N-M-N angles are 89.42(8)° for M = Cu and 89.5(1)° for M = Ni.

The 1-amidino-O-methylurea skeleton is nearly planar [rms deviation of atoms from the best least-squares plane of 0.029 Å (Cu complex) and 0.012 Å (Ni complex)] and lays close onto the core metal-N₄ plane.

As expected, the molecular skeleton of the saccharinate anion (sac) in both compounds is also nearly planar [rms deviation of atoms from the mean plane of 0.0209 Å (Cu complex) and 0.0119 Å (Ni complex)]. Saccharinate N-C and N-S bond distances of 1.337(3) and 1.614(3) Å in the Cu^{II} complex and of 1.334(4) and 1.625(3) Å in the Ni^{II} complex as well as the S-N-C angles (111.3(2)° (Cu) and 111.5(2)° (Ni)) are in good agreement with the corresponding distances and angles found in [M(nic)₂(H₂O)₄](sac)₂ (M = Co, Ni, Zn, nic = nicotinamide) [22] and [Fe(phen)₃](sac)₂(Hsac)·6H₂O [23].

The [Cu(cnge-OCH₃)₂]²⁺ and saccharinate planes subtend a dihedral angle of 14.9(1)° with each other and are arranged as a layered structure in the lattice. Each layer is further stabilized by a H-bonding network involving the cnge-OCH₃ skeleton, NH and terminal NH₂ groups as donors and the saccharinate carbonyl oxygen and nitrogen atoms as acceptors [d(N4···O3^{''}) = 2.796 Å, <(N4-H4···O3^{''}) = 155.3°, d(N3···N1^{''}) = 2.916 Å, <(N3-

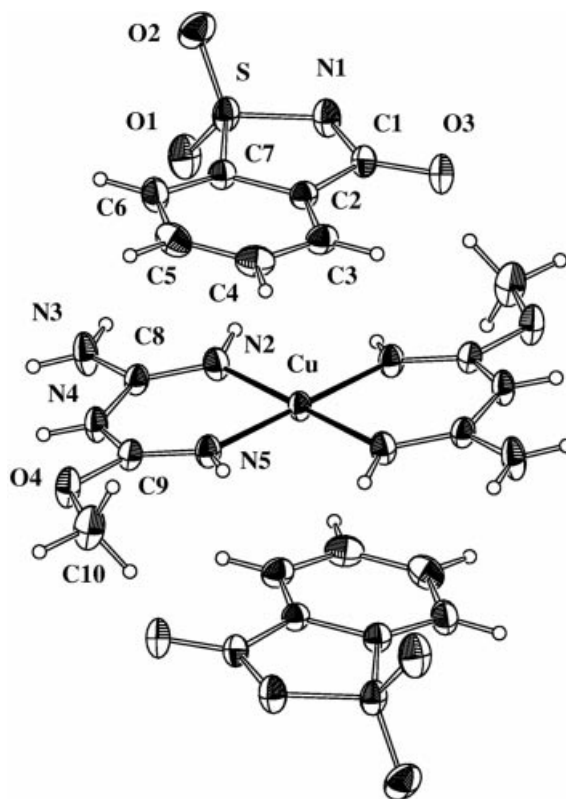


Fig. 1 View of the centrosymmetric [Cu(cnge-OCH₃)₂](sac)₂ complex showing the labels of the independent non-H atoms and their displacement ellipsoids at the 30% probability level. The metal complex and the saccharinate ions lay on adjacent sheets of the crystal layered structure.

H3A···N1[']) = 151.2°, d(N3···O3^{''}) = 2.819 Å, <(N3-H3B···O3^{''}) = 150.0°].

In the Ni^{II} complex, the [Ni(cnge-OCH₃)₂]²⁺ and saccharinate anions are nearly parallel to each other [angle of 4.1(1)° and the [Ni(cnge-OCH₃)₂](sac)₂ units are arranged along layers in the crystal. The units are further stabilized by a pair of N-H···N and N-H···O bonds involving as donors the cnge-OCH₃ skeleton, NH and terminal NH₂ groups and as acceptors the saccharinate nitrogen and carbonyl oxygen atoms [d(N4···N1[']) = 2.861, <(N4-H4N···N1[']) = 173.5°, d(N3···O3[']) = 2.860 Å, <(N3-H3B···O3[']) = 170.1°].

2.2 Electronic spectra and magnetic properties

The results of the measured electronic absorption and reflectance spectra are presented in Table 2. The electronic spectrum of the Cu^{II} complex clearly confirms the presence of a CuN₄ chromophore with a square planar geometry. In most of these chelate complexes the transitions from the d_{xy}, d_{z²} and d_{xz}, d_{yz} pair to the half-filled d_{x²-y²} level are expected as a broad envelope at about 520-550 nm [12, 24]. Besides, in the case of the Ni^{II} complex, the position of the four observed absorption bands and their intensities are

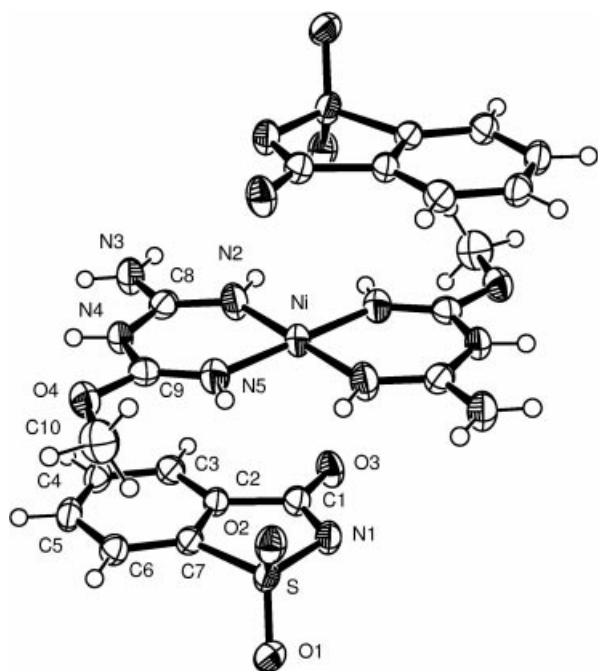


Fig. 2 Molecular plot of the $[\text{Ni}(\text{cnge-OCH}_3)_2](\text{sac})_2 \cdot 2\text{H}_2\text{O}$ solid at 120 K. Displacement ellipsoids are drawn at the 50% probability level.

Table 2 Electronic UV-vis and diffuse reflectance spectra of $[\text{Cu}(\text{cnge-OCH}_3)_2](\text{sac})_2$ (aqueous solution) (1) and $[\text{Ni}(\text{cnge-OCH}_3)_2](\text{sac})_2 \cdot 2\text{H}_2\text{O}$ ((1/1) ethanolic/aqueous solution) (2). (Band positions in nm).

	1	2
Diffuse reflectance	518 (broad)	410, 480, 660, 720
Electronic absorption spectra	550 (broad) (58.0)	412 (154) 514 (123) 602 (69.2) 674 (38.5)

in parenthesis, molar extinction coefficients in $\text{M}^{-1}\text{cm}^{-1}$.

characteristic for square planar complexes of this cation [25].

The diffuse reflectance spectra of both solids are similar to that found in solution, indicating that the same structures are retained upon dissolution.

The magnetic moments, measured at room temperature, are also in agreement with the geometry of both complexes. $[\text{Cu}(\text{cnge-OCH}_3)_2](\text{sac})_2$ presents a value of 1.93 BM that clearly corresponds to the presence of a single unpaired electron with a d^9 electronic configuration [26]. On the other hand, $[\text{Ni}(\text{cnge-OCH}_3)_2](\text{sac})_2 \cdot 2\text{H}_2\text{O}$ is diamagnetic, in agreement with the presence of a d^8 configuration in a square planar environment [26].

2.3 Infrared spectra

The assignment of some of the most characteristic IR bands of cyanoguanidine and of the new Cu^{II} and Ni^{II} complexes

Table 3 Assignment of the IR spectra of cyanoguanidine, $[\text{Cu}(\text{cnge-OCH}_3)_2](\text{sac})_2$ and $[\text{Ni}(\text{cnge-OCH}_3)_2](\text{sac})_2 \cdot 2\text{H}_2\text{O}$. (Band positions in cm^{-1}).

cnge	Ni/cnge-OCH ₃ /sac	Cu/cnge-OCH ₃ /sac	Assignments
3380 s	3512 m		$\nu(\text{OH})$, water
3337 s	3332 s	3317 s	$\nu_{\text{as}}(\text{N-H})$
3239 sh	3308 sh	3286 s	
3144 s	3222 m	3200 sh	
2212 s	3081 s	3082 s	$\nu_s(\text{N-H})$
2162 vs			$\nu(\text{C}\equiv\text{N})$
1662 sh	1678 vs	1670 s	$\nu(\text{C}=\text{N})$
1640 vs			
1574 s	1623 m	1611 m	$\nu(\text{C}=\text{O})$ sac
	1580 m	1564 m	$\delta(\text{N-H})$, cnge + (C-C) sac
1510 m	1550 sh	1541 sh	$\delta(\text{N-H})$, cnge
	1341 m	1352 m	$\nu(\text{CNS})$, sac
	1274 s	1266 s	$\nu_{\text{as}}(\text{SO}_2)$, sac
	1207 sh	1211 m	$\nu(\text{C-O-CH}_3)$
	1149 s	1144 s	$\nu_s(\text{SO}_2)$, sac

vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; br, broad.

are shown in Table 3. The main features are briefly commented as follows:

- The $\text{C}\equiv\text{N}$ stretching seen as a doublet at 2212/2162 cm^{-1} in free cyanoguanidine disappears upon coordination. Besides, a new band at 1211 cm^{-1} in the copper complex and at 1207 cm^{-1} in the nickel complex, can be assigned to the C-O-CH_3 stretching motion [27–29].
- The $\text{C}=\text{N}$ stretching vibrations suffer a small shift to higher frequencies after coordination, as has also been found in other similar complexes [12].
- The H_2O deformational mode of $[\text{Ni}(\text{cnge-OCH}_3)_2](\text{sac})_2 \cdot 2\text{H}_2\text{O}$ is probably overlapped by the medium 1623 cm^{-1} band of the saccharinate anion. The corresponding stretching vibrations are seen as a broad and medium intensity band centered at about 3510 cm^{-1} .
- The saccharinate bands are found in the same position as in sodium saccharinate [16], in agreement with the fact that it acts only as a counter anion in these complexes.

All these spectroscopic characteristics are in total agreement with the reported structural peculiarities of the two complexes.

2.4 Thermal behavior

The presence of hydration water molecules in the case of $[\text{Ni}(\text{cnge-OCH}_3)_2](\text{sac})_2 \cdot 2\text{H}_2\text{O}$ could be confirmed by its thermal behavior. The two water molecules are lost between 125 and 194 °C (weight loss found = 5.1%; calculated = 5.2%) After dehydration the TGA trace shows three additional steps, finally generating NiO (identified by IR spectroscopy) (observed weight loss = 89.0%; calculated = 89.2%).

In the case of $[\text{Cu}(\text{cnge-OCH}_3)_2](\text{sac})_2$ the thermal decomposition starts at 200 °C and occurs in six successive steps. The final residue was characterized by means of IR

spectroscopy as CuO (observed weight loss = 87.9 %; calculated = 88.0 %).

3 Experimental Part

3.1 Synthesis of the complexes

The starting material for the preparation of the two complexes were the Cu^{II} and Ni^{II} saccharinate complexes of composition [M(sac)₂(H₂O)₄]:2H₂O, obtained according to literature procedures [30, 31]. A methanolic solution of cyanoguanidine (2 mmol, 10 mL) was added to a suspension of 1 mmol of each of these complexes in 50 mL of methanol, and the mixture was refluxed. In the case of the Cu^{II} complex, a blue solution and a pink precipitate were obtained after 30 minutes. The precipitate was filtered off and washed several times with cold methanol. It was then redissolved in hot methanol and upon slow evaporation of the solution, good quality single crystals were obtained. Yield: 90 %. *Anal. Calcd.* For C₂₀H₂₄N₁₀O₈S₂Cu: C, 36.4; H, 3.6; N, 21.2; S, 9.7 %. *Found:* C, 36.5; H, 3.5; N, 21.3; S, 9.8 %.

For the Ni^{II} complex more drastic conditions were needed. The reflux was performed overnight and a few drops of NH₄OH were added to the reaction mixture. Yellow single crystals of [Ni(cnge-OCH₃)₂](sac)₂·2H₂O were obtained by slow and carefully evaporation of the resulting solution, with a very low yield (ca. 10 %). *Anal. Calcd.* For C₂₀H₂₈N₁₀O₁₀S₂Ni: C, 34.7; H, 4.0; N, 20.2; S, 9.2 %. *Found:* C, 34.9 %; H, 3.9; N, 20.3; S, 9.4 %.

3.2 Single crystal X-ray diffraction studies

Measurements were performed on a Kappa CCD diffractometer using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). For the Cu^{II} complex measurements were performed at 293 K, whereas for the Ni^{II} the working temperature was 120 K and a Oxford Cryosystem was used as low temperature device.

Programs used were COLLECT [32] for data collection and DENZO and SCALEPACK [33] for data reduction, SHELXS-97 [34] for structure solution and SHELXL-97 [35] for refinement. Intensities were corrected for Lorentz, polarization and absorption and in the case of the Cu^{II} complex also for extinction. The unit cells were obtained by least square refinement of the angular settings for 9927 reflections in the 2.84 < θ < 27.48° range for the Cu^{II} complex and for 10769 reflections in the 2.52 < θ < 24.99° range for the Ni^{II} complex.

The hydrogen atoms were positioned stereo-chemically and refined with the riding model. The methyl atom positions were refined by treating the CH₃ as a rigid group allowed to rotate around the corresponding C-C bond. The crystallization water molecules found in the nickel complex show positional disorder that could be modeled satisfactorily during the refinement in terms of two neighboring sites (about 1 Å apart) with occupancies that added up to one. As expected, the water H-atoms could not be located reliably in the residual electron density map.

The structures were solved by direct and Fourier methods and the final molecular models obtained by anisotropic full-matrix least-squares refinement of the non-hydrogen atoms.

Listing of atomic coordinates and equivalent isotropic displacement parameters, full intramolecular bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters are available from the authors and were deposited at the Cambridge Cry-

tallographic Data Centre, reference numbers CCDC-263107 ([Cu(cnge-OCH₃)₂](sac)₂) and CCDC-263108 ([Ni(cnge-OCH₃)₂](sac)₂·2H₂O).

3.3 Physicochemical measurements

Electronic absorption spectra were recorded on a Hewlett-Packard 8453 diode-array spectrophotometer, using 10 mm quartz cells. Electronic diffuse reflectance spectra were obtained with a Shimadzu UV-300 spectrophotometer, using MgO as a standard. Infrared spectra were recorded on a Perkin Elmer 580 B spectrophotometer using the KBr-pellet technique. Room temperature magnetic susceptibility was determined with a Cahn-2000 balance, calibrated with Hg[Co(SCN)₄], and at a magnetic field strength of 6 kG. Thermogravimetric measurements were performed on a Shimadzu model TG-50 TGA-system, using Pt-crucibles, working under an oxygen flow (50 mL/min) and at a heating rate of 10 °C/min. Sample quantities ranged between 5 and 10 mg. Elemental analyses for C, H, N and S were performed using a Carlo Erba EA 1108 analyzer.

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References

- [1] R. W. Miller, R. R. Eady, *Biochim. Biophys. Acta* **1988**, *952*, 290.
- [2] P. Ray, *Chem. Rev.* **1960**, *61*, 313.
- [3] P. J. Bailey, S. Pace, *Coord. Chem. Rev.* **2001**, *214*, 91.
- [4] M. J. Begley, P. Hubberstey, J. Stroud, *Polyhedron* **1997**, *16*, 805.
- [5] A. S. Batsanov, P. Hubberstey, C. E. Russell, P. H. Walton, *J. Chem. Soc. Dalton Trans.* **1997**, 2667.
- [6] A. S. Batsanov, P. Hubberstey, C. E. Russell, *J. Chem. Soc. Dalton Trans.* **1997**, 3189.
- [7] M. K. Ammar, F. B. Amor, T. Jouini, *J. Chem. Crystallogr.* **2002**, *32*, 87.
- [8] A. J. Blake, P. Hubberstey, W. Li, C. E. Russell, B. J. Smith, L. D. Wraith, *J. Chem. Soc. Dalton Trans.* **1998**, 647.
- [9] W. A. Baker, M. Daniels, *J. Inorg. Nucl. Chem.* **1963**, *25*, 1194.
- [10] R. L. Dutta, A. M. Singh, *J. Indian Chem. Soc.* **1975**, *52*, 1000.
- [11] R. L. Dutta, R. K. Ray, *J. Indian Chem. Soc.* **1976**, *53*, 507.
- [12] R. K. Ray, M. K. Bandyopadhyay, G. B. Kauffman, *Polyhedron* **1989**, *8*, 757.
- [13] U. Belluco, F. Benetollo, R. Bertani, G. Bombieri, R. A. Michelin, M. Mozzon, A. J. L. Pombeiro, F. C. Guedes da Silva, *Inorg. Chim. Acta* **2002**, *330*, 229.
- [14] A. D. Sadow, I. Haller, L. Fadinid, A. Togni, *J. Am. Chem. Soc.* **2004**, *126*, 14709.
- [15] E. J. Baran, *Quim. Nova*, in the press.
- [16] O. V. Quinzani, S. Tarulli, O. E. Piro, E. J. Baran, E. E. Castellano, *Z. Naturforsch.* **1997**, *52b*, 183.
- [17] P. A. M. Williams, E. G. Ferrer, M. J. Correa, E. J. Baran, E. E. Castellano, O. E. Piro, *J. Chem. Crystallogr.* **2004**, *34*, 285.
- [18] O. V. Quinzani, S. Tarulli, C. Marcos, S. Garcia-Granda, E. J. Baran, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1848.

- [19] B. S. Parajón-Costa, E. J. Baran, O. E. Piro, E. E. Castellano, *Z. Naturforsch.* **2002**, *57b*, 43.
- [20] O. V. Quinzani, S. Tarulli, S. García-Granda, C. Marcos, E. J. Baran, *Cryst. Res. Technol.* **2002**, *37*, 1338.
- [21] C. K. Johnson, ORTEP-II. A Fortran Thermal Ellipsoid Plot Program. Report ORLN-5318, Oak Ridge Natl. Laboratory, Oak Ridge, TN, 1976.
- [22] E. E. Castellano, O. E. Piro, B. S. Parajón-Costa, E. J. Baran, *Z. Naturforsch.* **2002**, *57b*, 657.
- [23] P. A. M. Williams, E. G. Ferrer, K. A. Pasquevich, E. J. Baran, E. E. Castellano, O. E. Piro, *J. Chem. Crystallogr.* **2000**, *30*, 539.
- [24] E. Prenesti, P.G. Daniele, M. Prencipe, G. Ostacoli, *Polyhedron* **1999**, *18*, 3233.
- [25] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, 2nd. Edit., Elsevier, Amsterdam, 1984.
- [26] F. A. Cotton, G. Wilkinson, C. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6th. Edit., J. Wiley & Sons, New York, 1999.
- [27] M. J. Begley, P. Hubberstey, *J. Chem. Res. (S)* **1982**, 118.
- [28] U. Kolodziej, J. Przyluski, *Polyhedron* **1985**, *4*, 395.
- [29] L. A. Sheludiyakova, E. V. Sobolev, A. V. Arbuznikov, E. B. Burgina, L. I. Kozhevina, *J. Chem. Soc. Faraday Trans.* **1997**, *93*, 1357.
- [30] S. Z. Haider, K. M. A. Malik, K. J. Ahmed, *J. Bangladesh Acad. Sci.* **1981**, *5*, 81.
- [31] S. Z. Haider, K. M. A. Malik, K. J. Ahmed, *Inorg. Synth.* **1985**, *23*, 47.
- [32] Enraf-Nonius, COLLECT, Nonius BV, Delft, The Netherlands, 2000.
- [33] Z. Otwinowski, W. Minor in: *Methods in Enzymology*, 276 (C. W. Carter, jr., R. M. Sweet, Eds.), Academic Press, New York, 1997, pp. 307–326.
- [34] G. M. Sheldrick, SHELXS-97. Program for Crystal Structure Resolution, University of Göttingen, Germany, 1997.
- [35] G. M. Sheldrick, SHELXL-97. Program for Crystal Structures Analysis, University of Göttingen, Germany, 1997.