Paramagnetic Octahedral *p*-Methoxyphenyldithiophosphonato Nickel(II) Complexes: Crystal Structures of $[Ni\{S_2P(OR)(p\text{-}CH_3O\text{-}C_6H_4)\text{-}\kappa S,S'\}_2(L\text{-}\kappa N)_2]$ ($R = Et, 2,4\text{-}{}^tBu_2C_6H_3$, L = 3-acetylpyridine)

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Dedicated to Professor Reinhard Schmutzler on the Occasion of his 70th Birthday

Abstract. The square-planar Ni^{II} complexes $[Ni\{S_2P(OR)(p\text{-}CH_3O\text{-}C_6H_4)\text{-}\kappa S,S'\}_2]$ react with 3-acetylpyridine to give green crystals of the paramagnetic octahedral complexes $[Ni\{S_2P(OR)(p\text{-}CH_3O\text{-}C_6H_4)\text{-}\kappa S,S'\}_2(L\text{-}\kappa N)_2]$ [R = Et (**1**), ${}^iPr$ (**2**), $2,4\text{-}{}^tBu_2C_6H_3$ (**3**); L = 3-acetylpyridine]. Complexes **1-3** were characterized by IR, MS, and UV-vis spectroscopy, and crystal structures were determined for **1** and **3**. The magnetic moments for **1-3** are 3.04-3.15 B.M.

Keywords: Dithiophosphonates; Octahedral paramagnetic nickel(II) complexes

Paramagnetische oktaedrische *p*-Methoxyphenyldithiophosphonato-nickel(II)-Komplexe: Molekülstrukturen von $[Ni\{S_2P(OR)(p\text{-}CH_3O\text{-}C_6H_4)\text{-}\kappa S,S'\}_2(L\text{-}\kappa N)_2]$ ($R = Et, 2,4\text{-}{}^tBu_2C_6H_3$, L = 3-Acetylpyridin)

Inhaltsübersicht. Die planar-quadratischen Ni^{II}-Komplexe $[Ni\{S_2P(OR)(p\text{-}CH_3O\text{-}C_6H_4)\text{-}\kappa S,S'\}_2]$ reagieren mit 3-Acetylpyridin zu den grünen paramagnetischen oktaedrischen Komplexen $[Ni\{S_2P(OR)(p\text{-}CH_3O\text{-}C_6H_4)\text{-}\kappa S,S'\}_2(L\text{-}\kappa N)_2]$ [R = Et (**1**), ${}^iPr$ (**2**), $2,4\text{-}{}^tBu_2C_6H_3$ (**3**), L = 3-Acetylpyridin]. Die Verbindungen **1-3** wurden durch IR- und UV-Vis-Spektroskopie, Massenspektrometrie und **1** und **3** auch durch Röntgenstrukturanalyse charakterisert. Das magnetische Moment von **1-3** beträgt 3.04-3.15 B.M.

1 Introduction

Complexes with dithiophosphato $[(RO)_2PS_2^-]$ [1, 2, 3, 4], dithiophosphinato $(R_2PS_2^-)$ [4, 5] and dithiophosphonato $[R'(RO)PS_2^-]$ [4, 6, 7, 8, 9, 10, 11, 12, 13] ligands have been utilized as insectizides, pestizides, flotation agents for mineral ores, solvent extraction reagents for metal ions and antioxidants. In the last few decades, many complexes with dithiophosphato and dithiophosphinato ligands were reported, but the number of dithiophosphonato complexes is limited because their synthesis is somewhat more challenging. Examples for the latter are the square-planar Ni^{II} dithiophosphonato complexes $[Ni\{S_2P(OR)(p\text{-}CH_3O\text{-}C_6H_4)\text{-}\kappa S,S'\}_2]$ in which the dithiophosphonates act as bidentate ligands [8, 10, 12]. These coordinatively unsaturated complexes react with donor molecules (L) to give paramagnetic octahedral Ni^{II} dithiophosphonato complexes $[Ni\{S_2P(OR)(p\text{-}CH_3O\text{-}C_6H_4)\text{-}\kappa S,S'\}_2(L)_2]$. Only a few complexes of this type are known up to now [8].

We now report the synthesis and spectroscopic properties of the paramagnetic octahedral complexes $[Ni\{S_2P(OR)(p\text{-}CH_3O\text{-}C_6H_4)\text{-}\kappa S,S'\}_2(L\text{-}\kappa N)_2]$ [R = Et (**1**), ${}^iPr$ (**2**), $2,4\text{-}{}^tBu_2C_6H_3$ (**3**); L = 3-acetylpyridine].

2 Results and Discussion

2.1 Synthesis and properties

The octahedral Ni^{II} dithiophosphonato complexes $[Ni\{S_2P(OR)(p\text{-}CH_3O\text{-}C_6H_4)\text{-}\kappa S,S'\}_2(L\text{-}\kappa N)_2]$ [R = Et (**1**), ${}^iPr$ (**2**), $2,4\text{-}{}^tBu_2C_6H_3$ (**3**); L = 3-acetylpyridine] were prepared by treating the square-planar Ni^{II} dithiophosphonato complexes $[Ni\{S_2P(OR)(p\text{-}CH_3O\text{-}C_6H_4)\text{-}\kappa S,S'\}_2]$ [10, 12] with 3-acetylpyridine in CH_2Cl_2/EtOH (3/1), as shown in Scheme 1. Complexes **1-3** are air-stable, slightly hygroscopic solids, but over several weeks they lose 3-acetylpyridine and reform the square-planar starting materials. They dissolve in $CHCl_3$ or CH_2Cl_2 to give purple solutions, indicative of square-planar nickel(II) complexes. However, ${}^{31}P$ NMR spectra of these solutions could not be obtained (even at

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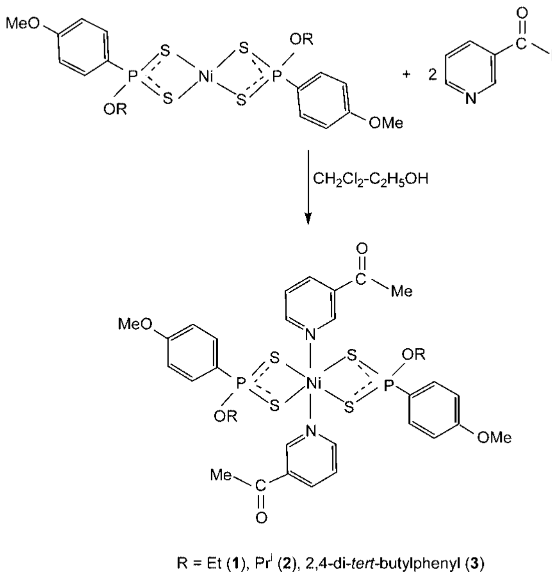
low temperature), and this indicates an equilibrium between the six- and four-coordinate complexes, as was also observed for related complexes [8].

Complexes **1-3** were characterized by elemental analysis (C, H, N, S), IR and UV-vis spectroscopy and mass spectrometry, and their magnetic moments were determined. Structural characterization of complexes **1** and **3** revealed axial coordination of two *N*-bonded monodentate 3-acetylpyridine ligands in octahedral Ni^{II} complexes. 2-Acetylpyridine does not react with $[Ni\{S_2P(OR)(p\text{-}CH_3O\text{-}C_6H_4)\text{-}\kappa S,S'\}_2]$, presumably due to steric hindrance.



Scheme 1

The IR spectra of complexes **1-3** show two bands at ca. 546 cm^{-1} and ca. 647 cm^{-1}, assigned to $\nu_{sym}(PS_2)$ and $\nu_{asym}(PS_2)$ vibrations, respectively [9]. The bands at about 1020 cm^{-1} can usually be assigned to the ν(PO) vibrations [13]. The mass spectra of **1**, **2** and **3** did not display molecular ion peaks (expected *m*/*z* 795, 873 and 1116); only the peaks arising from loss of two 3-acetylpyridine molecules are observed (*m*/*z* 552.3 (R = Et), 580.4 (R = ^iPr), and 872.7 (R = $2,4\text{-}^tBu_2C_6H_3$) for the corresponding nickel complexes $[Ni\{S_2P(OR)(p\text{-}CH_3O\text{-}C_6H_4)\text{-}\kappa S,S'\}_2]$).

2.2 *Molecular structures of 1 and 3*

Crystals of **1** and **3** were obtained from CH_2Cl_2/EtOH. The compounds crystallize in the monoclinic space group $P2_1/c$ with two centrosymmetric molecules in the unit cell. The nickel atom lies on a crystallographic center of inversion. In **1** (Fig. 1) and **3** (Fig. 2) the Ni^{II} ion is octahedrally coordinated by two bidentate dithiophosphonate ligands and two neutral monodentate *N*-bonded 3-acetylpyridine ligands in the axial positions.

In **1** and **3**, the P-S bond lengths of 198.6(1)-200.1(1) are similar to those of related complexes (Table 1) [8]. In **3**, the Ni-S [247.36(7), 252.80(8) pm (**1**) and 245.94(8), 248.00(8) pm (**3**)] and Ni-N bond lengths [222.7(2) (**1**), 216.4(2) pm (**3**)] are shorter than those in **1**, while the S-Ni-S [81.69(2) (**1**), 83.00(2)° (**3**)], N-Ni-S [90.68(6) (**1**), 92.48(6)° (**3**)], and S-P-S [109.89(4) (**1**), 110.34(4)° (**3**)] bond angles in **3** are larger than those in **1**, presumably due to the presence of the bulkier $2,4\text{-}^tBu_2C_6H_3$ group (Table 1).

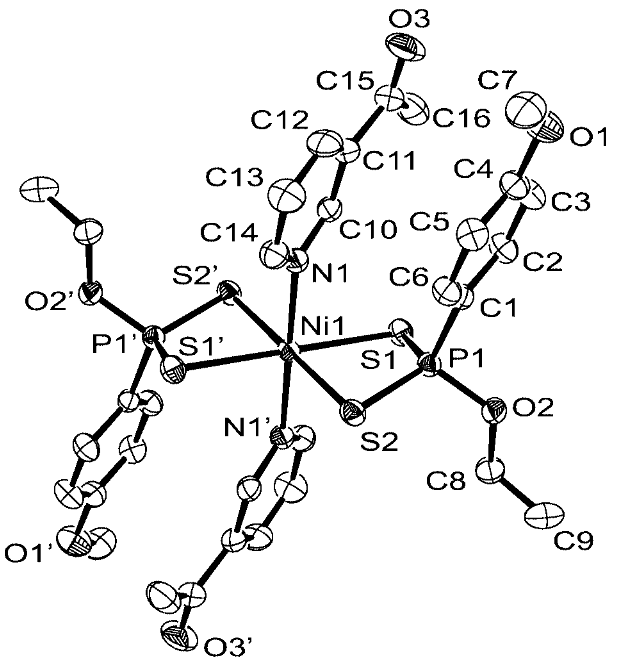


Figure 1 Molecular structure of **1** (ORTEP, 50 % probability, SHELXTL PLUS; XP [15], hydrogen atoms omitted for clarity).

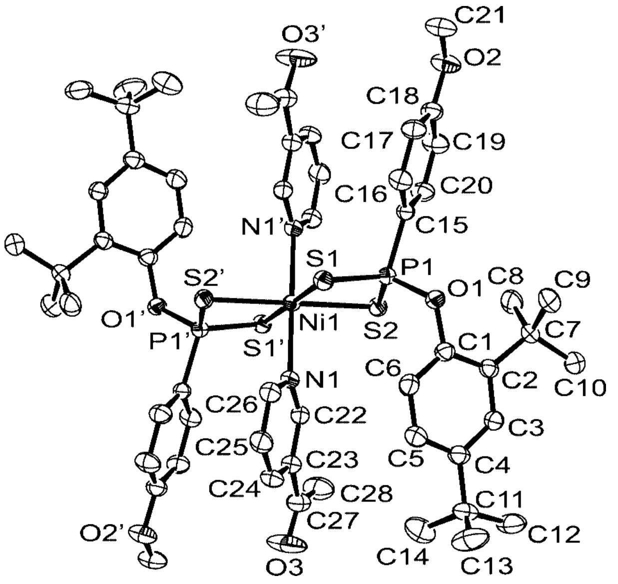


Figure 2 Molecular structure of **3** (ORTEP, 50 % probability, SHELXTL PLUS; XP [15], hydrogen atoms omitted for clarity).

Table 1 Selected bond lengths/pm and angles/deg for **1** and **3** and comparison with [Ni{$S_2P(OMe)(p\text{-}CH_3O\text{-}C_6H_4)$-κ*S,S'*}$_2$(L-κ*N*)$_2$] (L = pyridine (**I**), 4-NH_2-pyridine (**II**)) [8]

	1	**3**	**I**	**II**
Ni(1)-N(1)	212.7(2)	216.4(2)	212.5(3)	210.3(3)
Ni(1)-S(2)	247.36(7)	245.94(8)	249.4(1)	251.6(1)
Ni(1)-S(1)	252.80(8)	248.00(8)	250.4(1)	249.2(1)
S(1)-P(1)	199.8(1)	200.1(1)	198.7(1)	200.0(1)
S(2)-P(1)	199.9(1)	198.6(1)	199.8(1)	198.5(1)
N(1)-Ni(1)-S(2)	90.68(6)	92.48(6)	90.90(8)	90.76(9)
S(2)-Ni(1)-S(1)	81.69(2)	83.00(2)	81.68(4)	81.88(3)
S(2)-P(1)-S(1)	109.89(4)	110.34(4)	110.19(6)	110.91(5)

3 Experimental

Solvents were dried and distilled prior to use by standard methods. Compounds were handled with exclusion of air and moisture. Elemental analyses were determined with a VARIO EL (Heraeus). Mass spectra were recorded with a MAT-8230 (EI-MS, 70 eV). IR spectra were recorded as KBr disks with a Perkin-Elmer 2000 FT-IR spectrometer in the range 400-4000 cm^{-1}. The UV-vis spectra were recorded on a LAMBDA 900 (Perkin Elmer) spectrometer. Melting points (Gallenkamp) are uncorrected. The magnetic moments were determined with a magnetic susceptibility balance of Johnson Mathey Alfa Products. [Ni{$S_2P(OR)(p\text{-}CH_3O\text{-}C_6H_4)$-κ*S,S'*}$_2$] (R = Et, ^{i}Pr [10], 2,4-$^tBu_2C_6H_3$ [12]) were prepared according to literature procedures.

*General procedure for the preparation of **1-3**:*

0.1 g of the square-planar Ni^{II} complex [Ni{$S_2P(OR)(p\text{-}CH_3O\text{-}C_6H_4)$-κ*S,S'*}$_2$] was dissolved in CH_2Cl_2 (15 mL) and an excess of 3-acetylpyridine (1.5 mL) in EtOH (5 mL) was added. The purple solution was refluxed until it turned green. The solvent was evaporated at room temperature until 2 or 3 mL of solution remained. Green crystals were obtained from this solution, isolated, dried in vacuum and washed with diethyl ether.

3.1 trans-Bis{O-ethyl(4-methoxyphenyldithiophosphonato)-κS,S'}bis(3-acetylpyridine-κN)nickel(II) (**1**):

[Ni{$S_2P(OEt)(p\text{-}CH_3O\text{-}C_6H_4)$-κ*S,S'*}$_2$] (0.1 g, 0.18 mmol). Yield: 0.13 g (82 %); mp 121 °C. $C_{32}H_{38}N_2NiO_6P_2S_4$: calcd. C 48.31, H 4.81, N 3.52, S 16.12; found C 48.2, H 4.13, N 3.45, S 16.9 %.

EI MS: 552 $[M\text{-}2L]^+$ (100 %), 524 $[M\text{-}2L\text{-}C_2H_4]^+$ (10 %), 215 $[(MeOC_6H_4)PS_2O]^+$ (19 %), 155 $[(MeOC_6H_4)PO]^+$ (81 %), 139 $[(MeOC_6H_4)P]^+$ (44 %), 108 $[MeOC_6H_4]^+$ (58 %), and fragmentation products thereof (L = 3-acetylpyridine). **IR** (cm^{-1}): 1684vs, 1592vs, 1496s ν(CO), 1023vs ν(PO), 647s $\nu_{asym}(PS_2)$, 546vs $\nu_{sym}(PS_2)$. μ_{eff} = 3.15 B.M.. **UV-vis** spectrum: λ_{max} = 523 (ε = 84) and 697 nm (ε =168).

3.2 trans-Bis{O-isopropyl(4-methoxyphenyldithiophosphonato)-κS,S'}bis(3-acetylpyridine-κN)nickel(II) (**2**):

[Ni{$S_2P(O^iPr)(p\text{-}CH_3O\text{-}C_6H_4)$-κ*S,S'*}$_2$] (0.1 g, 0.17 mmol). Yield: 0.11 g (79 %); mp 127 °C. $C_{34}H_{42}N_2NiO_6P_2S_4$: calcd. C 49.58, H 5.14, N 3.40, S 15.57; found C 49.5, H 5.56, N 3.51, S 15.0 %.

Table 2 Crystal data and structure refinement for complexes **1** and **3**

	1	**3**
Empirical formula	$C_{32}H_{38}N_2NiO_6P_2S_4$	$C_{56}H_{70}N_2NiO_6P_2S_4$
Formula weight	795.53	1116.03
Temperature (K)	208(2)	213(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions		
a /pm	1095.3(2)	1116.8(2)
b /pm	1278.5(2)	2256.0(4)
c /pm	1425.6(2)	1210.4(2)
β /°	111.895(2)	110.133(3)
Volume /nm^3	1.8524(5)	2.8631(8)
Z	2	2
Density (calc.) /Mg/m^3	1.426	1.295
Absorption coefficient/mm^{-1}	0.879	0.590
F(000)	828	1180
Crystal size /mm^3	0.20 x 0.10 x 0.10	0.20 x 0.15 x 0.10
θ range for data collection /°	2.22 to 29.28	1.81 to 29.39
Index ranges	$-13<=h<=14$ $-16<=k<=15$ $-19<=l<=8$	$-14<=h<=10$ $-30<=k<=30$, $-13<=l<=16$
Reflections collected	10041	18046
Independent reflections	4518 [*R*(int) = 0.0391]	7128 [*R*(int) = 0.0479]
Absorption correction	SADABS	SADABS
Max. and min. transmission	0.9172 and 0.8438	0.9434 and 0.8912
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4518/0/290	7128/0/462
Goodness-of-fit on F^2	1.109	1.115
Final *R* indices [$I>2\sigma(I)$]	$R1 = 0.0549$ $wR2 = 0.0912$	$R1 = 0.0577$ $wR2 = 0.0978$
R indices (all data)	$R1 = 0.0820$ $wR2 = 0.0988$	$R1 = 0.0947$ $wR2 = 0.1087$
Largest diff. peak and hole /eÅ^{-3}	0.461 and −0.377	0.694 and −0.621

EI MS: 580 $[M\text{-}2L]^+$ (65 %), 538 $[M\text{-}2L\text{-}CMe_2]^+$ (15 %), 496 $[M\text{-}2L\text{-}2CMe_2]^+$ (96 %),275 $[(MeOC_6H_4)PS_2ONi]^+$) (19 %), 187 $[MeOC_6H_4POS]^+$ (34 %), 155 $[MeOC_6H_4PO]^+$ (100 %), 139 $[MeOC_6H_4P]^+$ (22 %), 108 $[MeOC_6H_4]^+$ (33 %), and fragmentation products thereof (L = 3-acetylpyridine). **IR** (cm^{-1}): 1696vs, 1592vs, 1498s ν(CO), 1020m ν(PO)?, 959 vs ν(PO)?, 647s $\nu_{asym}(PS_2)$, 546vs $\nu_{sym}(PS_2)$. $\mu_{eff} = 3.04$ B.M.. **UV-vis** spectrum: $\lambda_{max} =$ 524 ($\varepsilon = 70$) and 689 nm ($\varepsilon = 87$).

3.3 trans-Bis{O-2,4-di-tert-butylphenyl(4-methoxyphenyldithiophosphonato)-κS,S′}bis(3-acetylpyridine-κN)nickel(II) (**3**):

$[Ni\{S_2P(O\text{-}2,4\text{-}{}^tBu_2C_6H_3)(p\text{-}CH_3O\text{-}C_6H_4)\text{-}\kappa S,S'\}_2]$ (0.1 g, 0.11 mmol). Yield: 0.068 g (54 %); mp 120 °C. $C_{56}H_{70}N_2NiO_6P_2S_4$: calcd. C 60.26, H 6.32, N 2.50, S 11.49, found C 59.9, H 7.57, N 2.48, S 11.5 %.

EI MS: 873 $[M\text{-}2L]^+$ (28 %), 667 $[M\text{-}2L\text{-}O({}^tBu_2C_6H_3)]^+$ (18 %), 259 $[MeOC_6H_4PS_2Ni]^+$ (25 %), 191 $[{}^tBu_2C_6H_3]^+$ (100 %), 139 $[MeOC_6H_4P]^+$ (22 %), 57 $[C(CH_3)_3]^+$ (89 %), and fragmentation products thereof (L = 3-acetylpyridine). **IR** (cm^{-1}): 1684vs, 1592vs, 1497s ν(CO), 1023vs ν(PO), 648s $\nu_{asym}(PS_2)$, 547s $\nu_{sym}(PS_2)$. $\mu_{eff} = 3.14$ B.M.. **UV-vis** spectrum: $\lambda_{max} =$ 524 nm ($\varepsilon = 236$) and 682 nm ($\varepsilon = 264$).

*3.4 X-ray crystal structure determination of **1** and **3***

Crystallographic data are given in Table 2. Data [$\lambda(Mo_{K\alpha}) = 0.71073$ Å] were collected with a Siemens CCD (SMART) diffractometer. All observed reflections were used for determination of the unit cell parameters. Empirical absorption correction with SADABS [14]. The structure was solved by direct methods (SHELXTL PLUS [15]). H atoms located by difference maps and refined isotropically.

CCDC-231725 (**1**) and -231726 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or **deposit@ccdc.cam.uk**).

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References

[1] S. Ooi, Q. Fernando, *Inorg. Chem.* **1967**, *6*, 1558.
[2] M. D. Sexton, *J. Chem. Soc. Perkin Trans. 2*, **1984**, 1771.
[3] A. J. Burn, I. Gosney, C. P. Warrens, J. P. Wastle, *J. Chem. Soc. Perkin Trans. 2*, **1995**, 265.
[4] I. Haiduc, D. B. Sowerby, *Polyhedron*, **1995**, *15*, 2469.
[5] P. Porta, A. Sgamellotti, N. Vinciguerra, *Inorg. Chem.* **1971**, *10*, 541.
[6] W. E. van Zyl, R. J. Staples, J. P. Fackler, Jr., *Inorg. Chem. Commun.* **1998**, *1*, 51.
[7] J. P. Fackler, Jr., L. D. Thompson, Jr., *Inorg. Chim. Acta.* **1981**, *48*, 45.
[8] M. C. Aragoni, M. Arca, F. Demartin, F. A. Devillanova, C. Graiff, F. Isaia, V. Lippolis, A. Tiripicchio, G. Verani, *J. Chem. Soc. Dalton Trans.* **2001**, 2671.
[9] I. Haiduc, L. David, O. Cozar, R. Micu-Semeniuc, G. Mezei, M. Armenean, *J. Mol. Struct.* **1999**, *482-483*, 153.
[10] M. Arca, A. Cornia, F. A. Devillanova, A. C. Fabretti, F. Isaia, V. Lippolis, G. Verani, *Inorg. Chim. Acta.* **1997**, *262*, 81.
[11] C. M. Thomas, A. Neels, H. Stœckli-Evans, G. Süss-Fink, *J. Organomet. Chem.* **2001**, *633*, 85.
[12] Y. Özcan, S. Ide, M. Karakus, H. Yilmaz, *Acta Crystallogr.* **2002**, *C58*, m388.
[13] M. D. Santana, G. García, C. M. Navarro, A. A. Lozano, J. Pérez, L. García, G. López, *Polyhedron* **2002**, *21*, 1935.
[14] G. M. Sheldrick, SADABS − a Program for Empirical Absorption Correction, Göttingen, **1998**.
[15] SHELXTL PLUS, Siemens Analyt. X-ray Inst. Inc., **1990**, XS: Program for Crystal Structure Solution, XL: Program for Crystal Structure Determination, XP: Interactive Molecular Graphics.