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Inorganica Chimica Acta 359 (2006) 475–483
Inorganica Chimica Acta
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# Copper(I) complexes of *N*-thioacylamido(thio)phosphates and triphenylphosphine

Alexander Y. Verat [a,*], Felix D. Sokolov [a,*], Nail G. Zabirov [a], Maria G. Babashkina [a], Dmitry B. Krivolapov [b], Vasiliy V. Brusko [a], Igor A. Litvinov [b]

[a] *A.M. Butlerov Chemical Institute, Kazan State University, 18 Kremlevskaya street, Kazan 420008, Russian Federation*
[b] *A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Centre of the Russian Academy of Sciences, 8 Arbuzov street, Kazan 420088, Russian Federation*

Received 21 May 2005; received in revised form 21 September 2005; accepted 22 September 2005
Available online 28 November 2005

**Abstract**

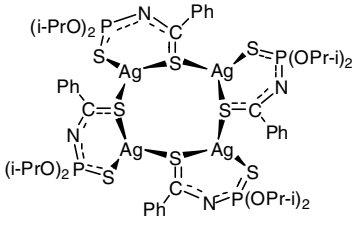
Heteroligand copper(I) complexes of bi- or bis-bidentate acylamidophosphates $PhC(S)NHP(S)(OPr\text{-}i)_2$, $PhC(S)NHP(O)(OPr\text{-}i)_2$, $Et_2NC(S)NHP(S)(OPr\text{-}i)_2$, $PhNHC(S)NHP(S)(OPr\text{-}i)_2$, *N*-(4-aminobenzo-15-crown-5)-$C(S)NHP(S)(OPr\text{-}i)_2$, *N*,*N*-(1,10-diaza-18-crown-6)-$[C(S)NHP(S)(OPr\text{-}i)_2]_2$, and triphenylphosphine were prepared and characterised. Copper is bound by two $PPh_3$ and one SCNPX (X = O, S) fragment of chelating ligand in all cases. Triphenylphosphine molecules reversibly dissociate in solution. Details of the X-ray structures of $(Ph_3P)_2Cu[PhC(S)NP(S)(OPr\text{-}i)_2]$ and $(Ph_3P)_2Cu[Et_2NC(S)NP(S)(OPr\text{-}i)_2]$ are reported.


*Keywords:* Copper complexes; *N*-phosphorylated thioureas; *N*-phosphorylated amides; Triphenylphosphine; Crystal structures

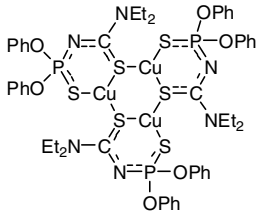
## 1. Introduction

*N*-(thio)phosphorylated (thio)amides (**1**) and *N*-(thio)phosphorylated (thio)ureas (**2**) are known to form complexes with a variety of metals both soft and hard. Many complexes of transition [1–5] and alkaline [5–9] metals with *N*-acylamidophosphinates (the general name of compounds containing XCNPY backbone) have been reported (see Scheme 1). Among them, transition metal complexes with C(S)NHP(S) ligands have been investigated most extensively.

Cu(I) and Ag(I) complexes with **1** and **2** are polynuclear in solid state. Thus, Ag(I) cations with thiobenzamide $PhC(S)NHP(S)(OPr\text{-}i)_2$ (**3**) form a tetrameric cyclic complex (**4**) [10]. The silver atom in **4** has trigonal configuration. A similar cyclic structure has been found in the trimeric complex of Cu(I) (**5**), obtained with the *N*-thiophosphorylated thiourea **2a** (both R = Et; R′ = OPh) [11]. The copper atoms of **5** adopt a trigonal configuration as well. The alteration in the ring size for **4** and **5** in comparison with each other can be explained both by the difference in ligand structure and in ionic radii of Cu(I) and Ag(I) cations.




**4**




**5**

Complexes of monovalent copper are of interest as catalysts of numerous processes including homolytic C–Hal (Hal = Cl, Br) bond cleavage in polyhaloalkanes [12]. *N*-thiophosphorylated bis-thioureas containing a crown ether

* Corresponding authors. Tel.: +7 8432 315310; fax: +7 8435 543754.
*E-mail addresses:* averat@mail.ru (A.Y. Verat), felix.sokolov@ksu.ru (F.D. Sokolov).

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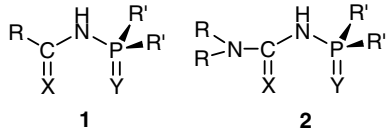
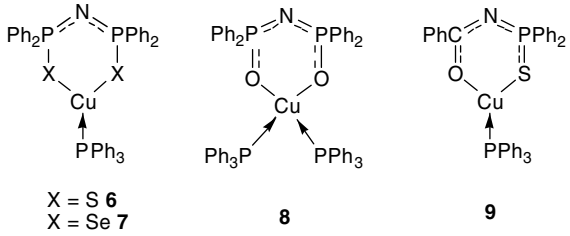
doi:10.1016/j.ica.2005.09.061



Scheme 1. General formula of *N*-(thio)phosphoryl(thio)amides (**1**) and *N*-(thio)phosphoryl(thio)ureas (**2**); X, Y = S, O; R′ = Ar, OAlk, OAr; R = H, Alk, Ar.

ring as a spacer are of special interest. The latter can participate in complexation by binding alkaline metal cations. Such complexes are interesting as potential binuclear complex catalysts, as models for studying redox processes within complexes, and as reagents for supramolecular synthesis [13].

Heteroligand copper(I) complexes of triphenylphosphine and XCNPY or XPNPX (X, Y = O, S, Se) backbone ligands (**6**–**9**) [5,14–16] have been earlier reported. (The style of representing the negative charge distribution through the XPNPX backbone in **6** and **7** was adopted from the papers cited.)



X = S **6**
X = Se **7**

**8**

**9**

Haiduc et al. [14] aimed to prepare the non-cluster complex of Cu(I), where the copper atom is bound only to one molecule of chelating SPNPS ligand. In this case, the filling of coordination sites of copper(I) is necessary to prevent cluster formation. The triphenylphosphine was used for this purpose. We conceived to employ an analogous method for synthesis of the complexes of crown containing thiophosphorylated thioureas.

Published data reveal that structure and properties of triphenylphosphine containing complexes **6**–**9** are strongly dependent on the nature of chelating ligand. That is why we at first prepared copper(I) complexes with thioacylamidothiophosphates and triphenylphosphine similar to **6**–**9**. Recently, we reported some synthetic results presented here as a preliminary communication [17]. Here we report the synthesis, characterization, and structure of complexes of triphenylphosphine and thiophosphorylated amides and ureas with copper(I). Structures of the obtained complexes are also discussed.

## 2. Experimental

### 2.1. General procedures

All solvents (except EtOH) were dried and distilled prior to use. Ethanol was of 95.6% grade and used without further purification. Infrared spectra (Nujol) were recorded on a Specord M-80 spectrometer in the 400–3600 $cm^{-1}$ range. NMR spectra of $CDCl_3$ solutions were obtained on a Varian Unity-300 NMR spectrometer at 25 °C. $^1H$, $^{31}P$, and $^{13}C$ chemical shifts, in ppm, were recorded at 299.948, 121.420, and 75.429 MHz, respectively. Chemical shifts are reported with reference to $SiMe_4$ ($^1H$ and $^{13}C$) and $H_3PO_4$ ($^{31}P$). Electron ionization mass spectra were recorded on a MKh-1310 instrument. Electron ionization energy was 70 eV and collector current was 30 μA. The substance was injected directly into the ion source at 100 °C. The exact values of molecular masses were determined automatically from the reference peaks of perfluorokerosene with the accuracy of no less than $5 \times 10^{-6}$ amu. ESI mass spectra were recorded on a Thermo Finnigan LCQ device. Concentrations were about $10^{-6}$ M (1:3 $CHCl_3/CH_3CN$), capillary temperature 210 °C. For complexes characterised by ESI in ionic clusters of particles containing three and more copper atoms the most abundant peaks in theory are mainly not the most intensive. This is due to overlapping of several closely located peaks. Here, we report masses of the most theoretically abundant peaks.

### 2.2. PhC(S)NHP(O)(OPr-i)$_2$ (*10*)

Synthesis of this compound was published for the first time in [18]. NaH (2.4 g, 0.1 mol) was added to a solution of thiobenzamide (6.85 g, 0.05 mol) in THF (100 ml). To the obtained suspension diisopropylchlorophosphate (10.02 g, 0.05 mol) was added dropwise. After it the precipitate of NaCl was filtered out, and the solvent was removed in vacuum. The residue was extracted with 1 N KOH solution. Water phase was separated and treated with $H_2SO_4$ (1 N solution) till reaching pH 1. Formed product was extracted with benzene, dried over $MgSO_4$, solvent was removed and residue was crystallized from benzene–hexane mixture (1:3). Yield: 3.0 g (20%). M.p. 134–135 °C. Calc. for $C_{13}H_{20}NO_3PS$ (301.09): C, 51.81; H, 6.69; P, 10.28; Found: C, 51.70; H, 6.82; P, 10.19%. $^{31}P\{^1H\}$ NMR ($CD_3CN$): $\delta = -7.00$. $^1H$ NMR ($CD_3CN$): $\delta = 1.27$ (d, $^3J_{HH} = 6.0$ Hz, 12H, $CH_3$), 4.74 (m, 2H, OCH), 7.34–7.80 (m, 5H, Ph), 9.50 (d, $^2J_{PNH} = 10.0$ Hz, 1H, NH). IR $\nu_{NH} = 3125$s, $\nu_{NCS} = 1500$m, $\nu_{CS} = 1346$w, $\nu_{PO} = 1274$m, $\nu_{P-O-C} = 1012$s br $cm^{-1}$.

### 2.3. Potassium salts of *3* and *10*

Synthesis of these compounds was published for the first time in [7]. *General procedure:* To the solution of 0.1 mol of **3** or **10** in 50–70 ml of methanol in three-necked flask, 0.1 mol of KOH in methanol was added dropwise whilst stirring. After completion of addition, the solution was stirred for 2 h, then methanol was removed at residual pressure 0.1 torr and at temperature 100–110 °C. The products were isolated as light-yellow powders. [PhC(S)NP(S)(OPr-i)$_2$]K: Yield 89%. M.p. 165–166 °C.

Calc. for $C_{13}H_{19}KNO_2PS_2$ (355.50): C, 43.92; H, 5.39; K, 11.00; P, 8.71; Found: C, 43.84; H, 5.53; K, 10.96; P, 8.78%. $^{31}P\{^1H\}$ NMR (acetone): $\delta = 67.00$. IR $\nu_{PNC} =$ 1435s, $\nu_{CS} = 1210$m, $\nu_{K\cdots O(P)-C} = 960$s, $\nu_{PS} = 625$w $cm^{-1}$. [PhC(S)NP(O)(OPr-i)$_2$]K: Yield 95%. M.p. 177 °C. Calc. for $C_{13}H_{19}KNO_3PS$ (339.05): C, 46.00; H, 5.54; K, 11.52; P, 9.13; Found: C, 45.77; H, 5.40; K, 11.56; P, 9.37%. $^{31}P\{^1H\}$ NMR (acetone): $\delta = 5.00$.

### 2.4. $Et_2NC(S)NHP(S)(OPr\text{-}i)_2$ (11)

A solution of diethylamine (0.365 g, 5 mmol) in benzene (25 ml) was added dropwise whilst stirring to a solution of SCNP(S)(OPr-i)$_2$ (1.2 g, 5 mmol) in benzene (15 ml). After an hour, benzene was partially removed in vacuum and reaction mixture became viscous. Then, *n*-hexane was added and after several days, colourless crystals began to form. Yield: 0.99 g (63%). $^{31}P$ NMR ($CCl_4 + C_6H_6$): $\delta = 59.98$. $^1H$ NMR ($CDCl_3$): $\delta = 1.30$ (br s, 6H, $CH_2CH_3$), 1.46 (d, $^3J_{HH} = 6.0$ Hz, 6H, $CH(CH_3)_2$), 1.47 (d, $^3J_{HH} =$ 6.1 Hz, 6H, $CH(CH_3)_2$), 3.66 (br s, 4H, $CH_2$), 4.98 (d sept, $^3J_{HH} = 6.2$ Hz, $^3J_{PH} = 10.6$ Hz, 2H, OCH). IR $\nu_{NH} = 3400$, $\nu_{NCS} = 1504$s, $\nu_{P-O-C} = 992$br, s, $\nu_{PS} = 648$m, $cm^{-1}$.

### 2.5. $(Ph_3P)_2Cu[PhC(S)NP(S)(OPr\text{-}i)_2\text{-}S,S']$ (12)

A solution of $(PPh_3)_2CuNO_3$ (0.34 g, 0.523 mmol) in $CH_2Cl_2$ (25 ml) was added dropwise whilst stirring to a solution of [PhC(S)NP(S)(OPr-i)$_2$]K (0.186 g, 0.523 mmol) in ethanol (25 ml). The mixture was stirred for an hour and precipitate was filtered off. The filtrate was concentrated until crystallization began. Isolated crystals were precipitated from a dichloromethane/*n*-hexane mixture 1:5 (v/v). Yield 0.32 g (70%). M.p. 143 °C. Calc. for $C_{49}H_{49}CuNO_2P_3S_2$ (904.52): C, 65.06; H, 5.46; Found: C, 65.57; H, 5.59%. $^1H$ NMR ($CDCl_3$): $\delta = 1.30$ (d, $^3J_{HH} = 6.4$ Hz, 6H, $CH_3$), 1.35 (d, $^3J_{HH} = 6.2$ Hz, 6H, $CH_3$), 4.90 (d sept, $^3J_{HH} = 6.2$ Hz, $^3J_{PH} = 10.1$ Hz, 2H, OCH), 7.03–7.76 (m, 35H, Ph). $^{31}P\{^1H\}$ NMR ($CH_2Cl_2$): $\delta = -0.62$ (2P, $PPh_3$), 54.76 (1P, NPS). IR $\nu_{NCS} = 1508$m, $\nu_{P-O-C} = 968$s, 990s, 1016s, $\nu_{PS} = 586$w $cm^{-1}$.

### 2.6. $(Ph_3P)_2Cu[Et_2NC(S)NP(S)(OPr\text{-}i)_2\text{-}S,S']$ (13)

To a suspension of $Et_2NC(S)NHP(S)(OPr\text{-}i)_2$ (**11**) (0.156 g, 0.5 mmol) in ethanol (25 ml) a KOH (0.5 mmol) solution in ethanol (15 ml) was added and the mixture was stirred until the ligand dissolved completely. To the resulting potassium salt, a solution of $(PPh_3)_2CuNO_3$ (0.325 g, 0.5 mmol) in $CH_2Cl_2$ (25 ml) was added dropwise. The mixture was stirred for an hour and a precipitate was filtered off. The filtrate was concentrated until crystallization began. Isolated crystals were precipitated from a dichloromethane/*n*-hexane mixture 1:5 (v/v) and used for a subsequent X-ray analysis. Yield 0.27 g (60%). M.p. 104 °C. Calc. for $C_{47}H_{54}CuN_2O_2P_3S_2$ (899.54): C, 62.76; H, 6.05; N, 3.11; P, 10.33; S, 7.13; Found: C, 62.25; H, 6.12; N, 3.45; P, 10.39; S, 6.45%. $^1H$ NMR ($C_6D_6$): $\delta = 1.26$ (t, $^3J_{HH} = 7.2$ Hz, 3H, $CH_2CH_3$), 1.37 (t, $^3J_{HH} = 7.2$ Hz, 3H, $CH_2CH_3$), 1.53 (d, $^3J_{HH} = 6.3$ Hz, 6 H, $CHCH_3$), 1.55 (d, $^3J_{HH} = 6.9$ Hz, 6H, $CHCH_3$), 3.67 (q, $^3J_{HH} = 7.0$ Hz, 2H, $CH_2$), 4.04 (q, $^3J_{HH} = 7.1$ Hz, 2H, $CH_2$), 5.19 (d sept, $^3J_{HH} + {}^3J_{PH} = 10.3$ Hz, 2H, OCH), 7.20–7.30 (m, 12H, Ph), 7.70–7.80 (m, 18H, Ph). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta = -0.70$ ($PPh_3$), 54.96 (NPS). IR $\nu_{NCS} =$ 1580m, $\nu_{P-O-C} = 970$–1030s, $\nu_{PC} = 690$m, $\nu_{PS} = 564$w $cm^{-1}$.

### 2.7. $(Ph_3P)_2Cu[PhNHC(S)NP(S)(OPr\text{-}i)_2\text{-}S,S']$ (14)

This was prepared similarly to compound **13** by using PhNHC(S)NHP(S)(OPr-i)$_2$ (**15**). Yield 42%. M.p. 146 °C. Calc. for $C_{49}H_{50}CuN_2O_2P_3S_2$ (919.53): C, 64.00; H, 5.48; N, 3.05; P, 10.11; S, 6.97; Found: C, 63.15; H, 6.02; N, 3.14; P, 10.77, S, 6.16%. $^1H$ NMR ($CDCl_3$): $\delta = 1.33$ (d, $^3J_{HH} = 6.3$ Hz, 6H, $CH_3$), 1.36 (d, $^3J_{HH} = 6.2$ Hz, 6H, $CH_3$), 4.79 (d sept, $^3J_{HH} = 6.2$ Hz, $^3J_{PH} = 10.6$ Hz, 2H, OCH), 7.08 (t, $^3J_{HH} = 7.1$ Hz, 1H, *p*-Ph), 7.24–7.50 (m, 32H, P–$C_6H_5$ and *o*-Ph), 7.57 (d, $^4J_{PNCNH} = 7.9$ Hz, 1H, NH), 7.73 (t, $^3J_{HH} = 8.4$ Hz, 2 H, *m*-Ph). $^{31}P$ NMR ($CDCl_3$): $\delta = -0.70$ ($PPh_3$), 54.96 (d t, $^3J_{POCH} + {}^4J_{PNCNH} = 9.3$ Hz, NPS $A_2MX$,). IR $\nu_{NH} = 3260$s, $\nu_{NCS} = 1538$m, $\nu_{P-O-C} = 984$br, $\nu_{PC} = 696$m, $\nu_{PS} = 560$w $cm^{-1}$.

### 2.8. $(Ph_3P)_2Cu[4\text{-}(1,2\text{-benzo-15-crown-5})NHC(S)NP(S)(OPr\text{-}i)_2\text{-}S,S']$ (16)

This was prepared similarly to compound **13** by using 4-(1,2-benzo-15-crown-5)NHC(S)NHP(S)(OPr-i)$_2$ (**17**). Yield 45%. M.p. 115–117 °C. $^1H$ NMR ($CDCl_3$): $\delta = 1.29$ (d, $^3J_{HH} = 8.4$ Hz, 6H, $CH_3$), 1.32 (d, $^3J_{HH} = 6.6$ Hz, 6H, $CH_3$), 3.78 (s, 8H, $PhOCH_2CH_2OCH_2CH_2$), 3.91 (m, 4H, $PhOCH_2CH_2$), 4.12 (m, 4H, $PhOCH_2$), 7.2–7.8 (m, 34H, $C_6H_5 + C_6H_3 +$ NH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -0.30$ ($PPh_3$), 54.5 (NPS). IR $\nu_{NCS} = 1480$m, $\nu_{P-O-C} = 980$–1020s, $\nu_{PS} = 600$m, 620m $cm^{-1}$.

### 2.9. $(Ph_3P)_2Cu[PhC(S)NP(O)(OPr\text{-}i)_2\text{-}O,S]$ (18)

This was prepared similarly to compound **12** by using potassium salt of **10**. Yield 86%. M.p. 161 °C. Calc. for $C_{49}H_{49}CuNO_3P_3S$ (888.45): C, 66.24; H, 5.56; N, 1.58; S, 3.61; Found: C, 66.76; H, 5.31; N, 1.68; S, 3.92%. $^1H$ NMR ($CDCl_3$): $\delta = 1.39$ (d, $^3J_{HH} = 6.3$ Hz, 6 H, $CH_3$), 1.43 (d, $^3J_{HH} = 6.3$ Hz, 6H, $CH_3$), 4,83 (d sept, $^3J_{HH} + {}^3J_{PH} = 6.7$ Hz, 2H, OCH), 7.24–7.86 (m, 35H, $C_6H_5$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 4.70$ (1P, PO), −3.62 (2P, $PPh_3$). IR $\nu_{NCS} = 1500$m, $\nu_{PO} = 1176$m, $\nu_{P-O-C} = 1020$s br $cm^{-1}$.

### 2.10. $(Ph_3P)_4Cu_2\{1,10\text{-diaza-18-crown-6}[C(S)NP(S)(OPr\text{-}i)_2]_2\text{-}S,S',S'',S'''\}$ (19)

This was prepared similarly to compound **13** using 1,10-(diaza-18-crown-6)-[C(S)NHP(S)(OPr-i)$_2$]$_2$ (**20**), a double amount of KOH, and $(PPh_3)_2CuNO_3$. Yield 76%. M.p.

144–145 °C. Calc. for $C_{98}H_{112}Cu_2N_4O_8P_6S_4$ (1915.16): C, 61.46; H, 5.89; N, 2.93; P, 9.70; S, 6.70; Found: C, 61.22; H, 5.82; N, 2.77; P, 10.15; S, 6.34%. $^1$H NMR ($CDCl_3$): $\delta = 1.28$ (d, $^3J_{HH} = 6.3$ Hz, 12H, $CH_3$), 1.36 (d, $^3J_{HH} = 6.0$ Hz, 12H, $CH_3$), 3.59–3.65 (m, 8H, $NCH_2$), 3.75 (t, $^3J_{HH} = 6.3$ Hz, 4H, $NCH_2CH_2O$), 3.85 (t, $^3J_{HH} = 5.4$ Hz, 4H, $NCH_2CH_2O$), 3.96 (t, $^3J_{HH} = 5.8$ Hz, 4H, $OCH_2CH_2O$), 4.21 (t, $^3J_{HH} = 5.4$ Hz, 4H, $OCH_2$-$CH_2O$), 4.73 (d sept, $^3J_{HH} + {}^3J_{PH} = 8.7$ Hz, 4H, OCH (Pr-i)), 7.32–7.76 (m, 60H, P–$C_6H_5$). $^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta = -0.60$ ($PPh_3$), 51.51 (s, NPS). IR $\nu_{NCS} =$ 1480m, $\nu_{P\text{-}O\text{-}C} = 1000$br, s, $\nu_{PC} = 696$m, $\nu_{PS} = 575$w cm$^{-1}$.

### 2.11. X-ray crystallography

The X-ray diffraction data for the crystals of **12** and **13** were collected on a Enraf-Nonius CAD4 automatic diffractometer using graphite monochromated Mo Kα (0.71073 Å) radiation. The details of crystal data, data collection, and the refinement are given in Table 1. The stability of crystals and experimental conditions was checked every 2 h using three control reflections, while the orientation was monitored every 200 reflections by centering two standards. No significant decay was observed. The structure was solved by direct method using the SIR [19] program and refined by the full matrix least-squares using the program SHELXL-97 [20]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated position with thermal parameters 30% larger than atom to which they attached. All calculations were performed on PC using WINGX [21] program. Cell parameters, data collection and data reduction were performed on Alpha Station 200 computer using MOLEN [22] program. All figures were made using the program ORTEP [23].

Table 1
Crystallographic data for complexes **12** and **13**

| | **12** | **13** |
|---|---|---|
| Chemical formula | $C_{49}H_{49}CuNO_2P_3S_2$ | $C_{47}H_{54}CuN_2O_2P_3S_2$ |
| Crystal habit | yellow prism | colorless prism |
| Crystal size (mm) | 0.4 × 0.4 × 0.4 | 0.4 × 0.35 × 0.35 |
| Formula weight | 904.46 | 899.49 |
| Crystal system | triclinic | monoclinic |
| Space group | $P\bar{1}$ | $P2_1/n$ |
| $a$ (Å) | 12.092(2) | 13.058(2) |
| $b$ (Å) | 12.053(2) | 20.931(2) |
| $c$ (Å) | 18.899(4) | 17.560(6) |
| $\alpha$ (°) | 98.25(2) | 90.00 |
| $\beta$ (°) | 104.12(2) | 109(2) |
| $\gamma$ (°) | 114.65(2) | 90.00 |
| $V$ (Å$^3$) | 2332.26 | 4538(1) |
| $Z$ | 2 | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 1.29 | 1.32 |
| $F$(000) | 944 | 1888 |
| Radiation (Å) | Mo Kα (0.71073) | Mo Kα (0.71073) |
| Temperature (K) | 293 | 293 |
| Scan mode | $\omega/2\theta$ | $\omega/2\theta$ |
| Recording range $\theta_{max}$ (°) | 22.76 | 23.87 |
| Absorption correction | Not applied | $\psi-$scans |
| $\mu$ (cm$^{-1}$) | 7.0 | 7.2 |
| Scan speed (deg min$^{-1}$) | Variable, 1–16.4 | Variable, 1–16.4 |
| Reflections measured | 5761 | 3298 |
| No. of independent reflections with $F^2 \geqslant 4\sigma(F^0)$ | 5556 | 2241 |
| $R$ (%) | 0.039 | 0.040 |
| $R_w$ (%) | 0.099 | 0.066 |
| $S$ | 1.03 | 1.02 |

## 3. Results and discussion

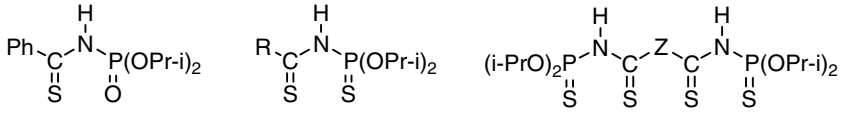
### 3.1. Synthesis

*N*-diisopropoxyphosphorylthiobenzamide **10** has been obtained by the reaction of thiobenzamide with diisopropylchlorophosphate in the presence of NaH. *N*-diisopropoxythiophosphorylthiobenzamide **3** was prepared according to the previously described method [24]. Thiophosphorylated thioureas **11**, **15**, **17**, **20**, and **21** (Scheme 2) were prepared by addition of the corresponding amine to diisopropylthiophosphoryl isothiocyanate [1,25,26].

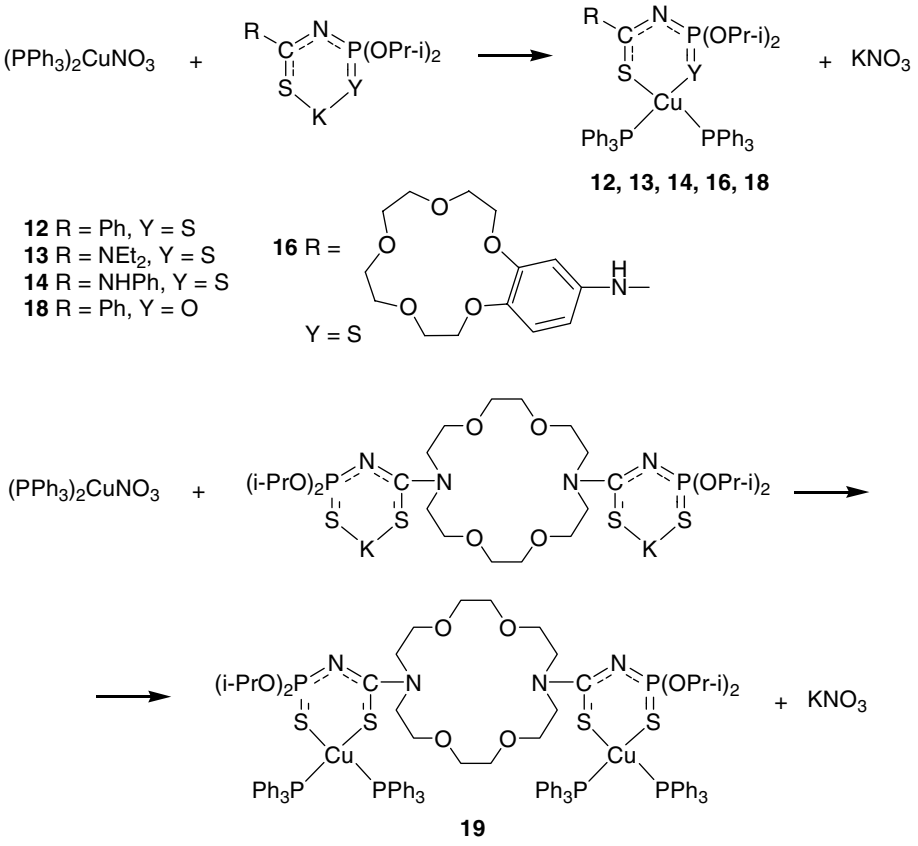
Heteroligand copper(I) complexes were prepared by the metathesis reaction between the potassium salts of ligands and $Cu(PPh_3)_2NO_3$ (Scheme 3).

Obtained complexes have been crystallized from $CH_2Cl_2$–hexane solutions. They are readily soluble in $CH_2Cl_2$, $CHCl_3$, acetone, and benzene, poorly soluble in $C_2H_5OH$, *i*-$C_3H_7OH$ and insoluble in hexane. The compounds have been characterized by IR, NMR $^1$H and $^{31}$P spectroscopy, two of them have been studied by X-ray crystallography. We also tried to use $(PPh_3)_3CuBr$ as a starting material, but in this case it is necessary to separate free triphenylphosphine emerges and so we decided to utilize $Cu(PPh_3)_2NO_3$.

Reaction of $(PPh_3)_2CuNO_3$ with the potassium salt of bis-thiourea **21** along with the target complex affords byproducts. $^{31}$P NMR spectrum of the isolated mixture contains resonances at 54.82 (84.0%), 60.15 (5.0%), 51.95 (7.5%) and 43.87 ppm (3.5%). The most intensive signal was ascribed to the thiophosphoryl group of the expected complex (**22**) (Scheme 4) by comparison with the stable complexes **12**–**14**, **16**; the resonance at 60.15 ppm corresponds to the imidothiophosphate $(R_2N)_2C{=}N$–$P(S)(OPr\text{-}i)_2$ (**23a** and **23b**) environment of phosphorus atom [27]; the resonance at 51.95 ppm corresponds to the amidothiophosphate environment of phosphorus (**24**) and the resonance at 43.87 ppm is due to the thiophosphorylisothiocyanate $SCNP(S)(OPr\text{-}i)_2$ (**25**). The $^1$H NMR spectrum also contains signals of low intensity, which correspond to the products of ligand decomposition. In the IR spectrum of the mixture there is a strong broad band in the range 1600–1650 cm$^{-1}$, which has been ascribed to the stretching vibration of C=N group. Such decomposition processes which proceed via *N*-thiophosphoryl-*N*′-phenylcarbodiimide $(RO)_2P(S)N{=}C{=}NPh$ (**26**) have been previously observed for a number of complexes of phosphorylated thioureas [1,28–30]. Scheme 4 illustrates




Scheme 2. Parent *N*-acylamido(thio)phosphates. R = Ph (**3**), $NEt_2$ (**11**), NHPh (**15**), 4-aminobenzo-15-crown-5 (**17**), *Z* = 1,10-diaza-18-crown-6 (**20**), $HN(CH_2)_2O(CH_2)_2NH$ (**21**).




Scheme 3. Synthesis of complexes.

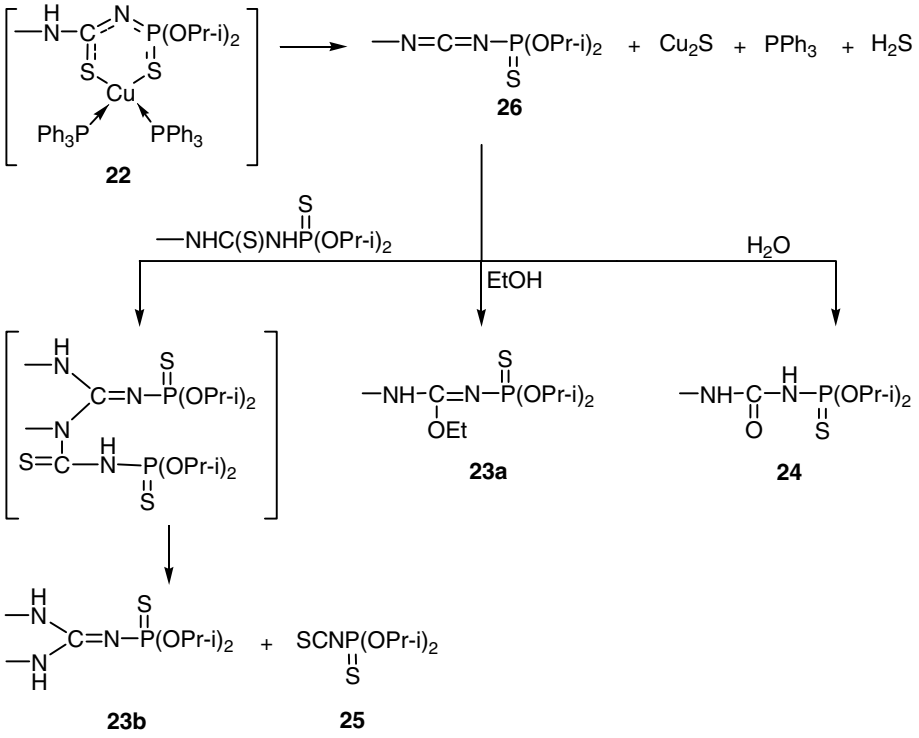
in generalized fashion the decomposition process of the complex.

NMR and IR spectra of the complex **16** contain signals or bands of small intensity, which correspond to the decomposition products shown in the Scheme 4. Because **16** is not pure, according to the spectral data, the elemental analysis has not been performed. It was also observed that after several days in $CHCl_3$ at 25 °C the solution of **16** is mainly decomposed. This results in an increase in the signals of the starting ligand **17** and O=$PPh_3$ resonances in $^{31}P$ NMR spectra (at 53.2 and 29.5 ppm, respectively). Overall, complex **16** has greater stability than the complex formed by bis-urea **21**. Decomposition of complex **14**, which also contains the NHCS fragment, was not observed.

### 3.2. Mass-spectroscopy

Electron ionization mass spectra of the complexes **12**–**14** and **18** do not demonstrate peaks corresponding to the molecular ion. In the mass spectrum of **13**, there are peaks of the monomeric complex $[CuL]^+$ cation (*m*/*z* 374.2, 21%) and of dimeric one $[Cu_2L_2]^+$ (*m*/*z* 750.5, 25%). (Here, HL and $H_2L$ are neutral ligands and L is its deprotonated form.) The spectrum also shows peaks of $HL^+$ (*m*/*z* 312.2 8%) and $L^+$ (*m*/*z* 311.3, 11%) cations. In the spectrum of **14**, along with the peak of complex cation $[CuL]^+$ (*m*/*z* 394, 5%), the peaks of carbodiimide $[PhN{=}C{=}NP(S)(OPr\text{-}i)_2]^+$ (*m*/*z* 298.2, 100%) and of $HL^+$ (*m*/*z* 332.2, 45%) are present. The carbodiimide peak is even more intense than $PPh_3$ one, again stressing the trend of complexes (and ligands) containing the RNH– group at carbamide carbon to form carbodiimides.

Electrospray ionization mass spectra of the complexes **12**, **14** and **19** also do not contain molecular ion peaks. This fact is an evidence for dissociation of labile Cu–$PPh_3$ bond at high dilution and high temperature conditions. The spectra of the complexes **12**, **14** and **19**, however, show the presence of peaks due to species formed in a $PPh_3$ dissociation process. These are: $[CuLPPh_3 + H]^+$ for **12** and **14** (*m*/*z*




Scheme 4. Decomposition processes in the complexes of the phosphorylated thioureas containing RNHCS moiety.

642.0, 4.4% and *m/z* 657.0, 7.8%, respectively) and $[Cu_2LPPh_3]^+$ (*m/z* 1126.6, 1.2%) for **19**. Spectra of **12** and **14** contain peaks of $[Cu_{n+1}L_n]^+$ ions. For the **12**: $[Cu_3L_2]^+$ (*m/z* 822.7, 25.6%), $[Cu_4L_3]^+$ (*m/z* 1201.7, 100%), $[Cu_5L_4]^+$ (*m/z* 1581.0, 0.44%) and for the **14**: $[Cu_3L_2]^+$ (*m/z* 852.8, 31.7%), $[Cu_4L_3]^+$ (*m/z* 1246.8, 100%), $[Cu_5L_4]^+$ (*m/z* 1640.2, 4.7%). Such a high intensity of the $[Cu_4L_3]^+$ ions is caused by their stability. We suggest these ions have cluster structure like the cation $[Cu_4\{(SPPh_2)_2N\}_3]^+$ [31]. The $[Cu_3L_2]^+$ and $[Cu_5L_4]^+$ ions probably also have a cluster structure, for example the $[Cu_5L_4]^+$ ions may originate from tetramers like **4**. Diazacrown containing complex **19** shows a peak assignable to $[Cu_2L + H]^+$ (*m/z* 866.9, 70.7%) and peaks where metal cations are trapped by the crown ether ring: $[Cu_2L + Na]^+$ (*m/z* 889.0, 100%) and $[Cu_3L]$ (*m/z* 928.9, 5.7%). Furthermore, the spectrum of **19** shows peaks of $[Cu_4L_2]^+$ (*m/z* 1730.8, 1.9%) and of $[Cu_5L_2]^+$ (*m/z* 1793.0, 2.6%). In this case the extra Cu(I) ions are probably bound by crown rings and are likely to form cluster centers.

### 3.3. IR and NMR spectroscopy

The IR spectra of copper complexes exhibit absorption bands at the ranges 1490–1580, 970–1030 and 690–696 $cm^{-1}$, which were assigned to the group and stretching vibrations of SCN, POC and P–C (P–Ph) groups, respectively. The P=S absorption band shifts to lower frequency from 620–648 in parent ligands to 560–600 $cm^{-1}$ in the complexes. In complex **18**, the P=O vibration is observed at 1176 $cm^{-1}$ and shifts to lower frequencies in comparison with the free ligand **10** (1252 $cm^{-1}$). Absorption band of phosphorylamide NH group disappears under complexation.

The $^1H$ NMR spectra of the complexes contain the only signals which corresponds to the proposed structure. Signals of $Et_2N$ group in **13** are doubled due to hindered rotation. The spectrum of **19** shows more signals in the region of crown ether ring than the expected number of nonequal protons, this is evidence for the crown ether ring having different conformers in solution. Methyl protons in isopropyl groups are diastereotopic and show two signals in spectra. A rather high $^4J_{PNCNH}$ coupling constant (7.9 Hz) in **14** was already observed for Cd, Zn, Pd and Ni, complexes of the ligand **15** [4]. It was explained by the fact that the PNCNH chain in these complexes meets the so-called *W*-criterion [32]. The resonance at 51.4–55.0 ppm in $^{31}P$ NMR spectra of **12**–**14**, **16**, and **19** corresponds to the phosphorus of thiophosphoryl group. The resonance of the phosphoryl phosphorus in **18** appears at 4.70 ppm and is shifted to low field in comparison with the free ligand **10** (−7 ppm). The signals of triphenylphosphine are observed from −0.3 to −3.62 ppm, and occur downfield of free $PPh_3$. Triphenylphosphine signals in the complexes **12**–**14**, **16**, and **19**, which contain thiophosphoryl groups have a chemical shift found to be very close to that in the trigonal complex **6** (−0.7 ppm) [14].

Fast exchange between free and bound triphenylphosphine in solutions of studied complexes results in phosphine signal broadening in $^{31}P$ NMR spectra, as was observed for the Cu(I) thioether complexes (see [33] and

references therein). An exchange equation can be written as follows:

$$Cu[RC(S)NP(S)(OPr\text{-}i)_2]\,(PPh_3)_2 \rightleftarrows Cu[RC(S)NP(S)(OPr\text{-}i)_2]PPh_3 + PPh_3$$

Peak widths of signals at half height maximum are in the range 30–50 Hz. This broadening affords the infringement of the ratio of integral intensity of the signals of triphenylphosphine and thiophosphoryl groups. For instance, in the compound **14** the integral intensity of the $PPh_3$ phosphorus is 1.47 times higher than it is for the thiophosphoryl phosphorus. At the same time, the ratio of intensity of the phosphine phosphorus to the phosphoryl one is exactly 2:1 in the **13**, **16** and **18**. A similar drawback is absent in the proton spectra. The ratio of integral intensity of phenyl protons to the alkyl protons in the $^1H$ NMR spectra reveals the composition of phosphorylthiourea: $PPh_3 = 1{:}2$ for complexes **12**–**14**, **16**, **18**, and 1:4 for the **19**.

### 3.4. Crystal structure of complexes *12* and *13*

The molecular structures of **12** and **13** are shown in Figs. 1 and 2, respectively. Selected bond lengths, bond and torsion angles are given in Table 2. The geometry around the Cu atom is tetrahedral in both complexes formed by two sulfurs and two $PPh_3$. The values of bond angles around Cu are in the range from 103.14(4)° to 119.58(5)° and from 105(2)° to 116(2)° for **12** and **13**, respectively. P–Cu bonds are longer than they are in the trigonal complexes **6**, **7**, **9** (2.216, 2.222, 2.190 Å, respectively) and tetrahedral **8** (2.255 and 2.245 Å). The difference in P–Cu bond lengths in comparison with trigonal complexes testifies for some sterical hindering of triphenylphosphine molecules. An example of stronger hindrance is a $(PPh_3)_3CuI$ molecule: Cu–P bond length is 2.362 Å [34].

P–S and C–S bonds are longer while P–N and C–N are shorter in comparison to those for the free ligand **3** [35], and have intermediate bond order values between the double and the single. The six-membered CuSPNCS metallocycle in **12** has the conformation of a distorted boat with the

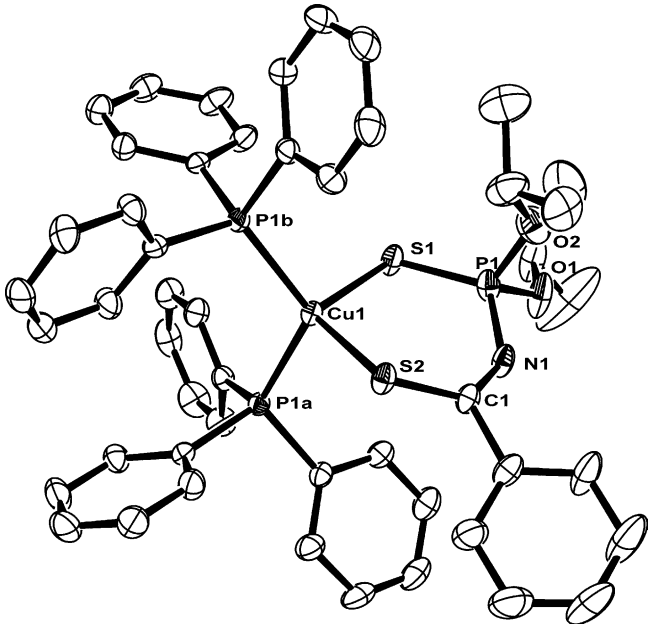



Fig. 1. ORTEP view of $(Ph_3P)_2Cu[PhC(S)NP(S)(OPr\text{-}i)_2]$ **12**.

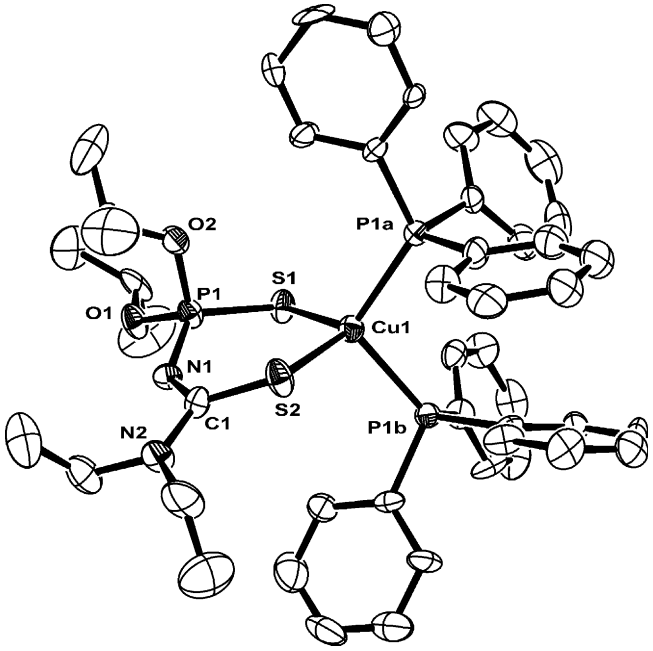



Fig. 2. ORTEP view of $(Ph_3P)_2Cu[Et_2NC(S)NP(S)(OPr\text{-}i)_2]$ **13**.

Table 2
Selected bond distances (Å), bond and torsion angles (°) for compounds **12** and **13**

| | **12** | **13** |
|---|---|---|
| Cu(1)–S(1) | 2.356(1) | 2.337(2) |
| Cu(1)–S(2) | 2.299(1) | 2.304(2) |
| Cu(1)–P(1a) | 2.311(1) | 2.302(2) |
| Cu(1)–P(1b) | 2.280(1) | 2.335(2) |
| S(1)–P(1) | 1.965(1) | 1.980(3) |
| S(2)–C(1) | 1.715(4) | 1.727(9) |
| P(1)–N(1) | 1.593(3) | 1.575(7) |
| N(1)–C(1) | 1.290(5) | 1.32(1) |
| S(1)–Cu(1)–S(2) | 107.09(4) | 108(2) |
| S(1)–Cu(1)–P(1a) | 103.74(5) | 116(2) |
| S(1)–Cu(1)–P(1b) | 107.65(4) | 105(2) |
| S(2)–Cu(1)–P(1a) | 103.14(4) | 111(2) |
| S(2)–Cu(1)–P(1b) | 114.58(4) | 108(2) |
| P(1a)–Cu(1)–P(1b) | 119.58(4) | 109(2) |
| Cu(1)–S(1)–P(1) | 103.30(5) | 98(2) |
| Cu(1)–S(2)–C(1) | 109.0(1) | 111(2) |
| S(1)–P(1)–N(1) | 120.8(1) | 123(2) |
| P(1)–N(1)–C(1) | 134.3(3) | 130(2) |
| S(2)–C(1)–N(1) | 129.4(3) | 128(2) |
| S(1)–P(1)–N(1)–C(1) | −41.0(5) | 55(2) |
| P(1)–N(1)–C(1)–S(2) | 0.2(6) | −8(2) |
| P(1)–N(1)–C(1)–C(2) | −176.4(3) | |
| P(1)–N(1)–C(1)–N(2) | | 173(2) |

Table 3
Deviations of atoms from the least square plane of the CuSPNCS cycle in **12** and **13**

| | 12 | 13 |
|---|---|---|
| Cu | −0.139(1) | 0.027(2) |
| S(1) | −0.158(2) | 0.275(3) |
| P(1) | 0.295(2) | −0.362(3) |
| N(1) | −0.137(4) | 0.148(7) |
| C(1) | −0.159(4) | 0.154(9) |
| S(2) | 0.297(2) | −0.242(3) |

P(1) and S(2) atoms showing the greatest deviation from the least square plane of the CuSPNCS cycle (Table 3). A conformation of the CuSPNCS cycle in **13** is nearly identical. The fragments CC(S)NP in **12** and NC(S)NP in **13** are almost planar, the sulfur of thiophosphoryl group is significantly deviated from the average planes of these fragments. This deviation of the phosphoryl sulfur is common for the complexes of *N*-thioacylamidophosphates [3,6,7,36].

## 4. Conclusion

*N*-acylamidophosphates which have been studied form stable crystalline complexes with Cu(I) cations of the general composition $LCu(PPh_3)_2$. These complexes dissociate in solutions, splitting off a molecule of triphenylphosphine. This process has reversible character.

Electronic properties and steric requirements of coordinating ligands influence the coordination number of copper(I). This was clearly shown in the example of Cu(I) phosphine complexes of poly(pyrazolyl)borates [37]. Silvestru et al. [16] have noted that in parallel with the electronic reasons, the large bite of chelating ligands in **6** and **7** can result in displacement of the coordinated triphenylphosphine and formation of trigonal complexes. Electronic properties of chelating ligands reported here and those in the complexes **6**–**9** are too different to compare, but taking into account small triphenylphosphine hindrance in the complexes described here, this reason itself can also explain their coordination number.

## 5. Supplementary material

Crystallographic data for the structural analyses with thermal parameters and complete tables of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). The data are available on request on quoting CCDC-254580 and 254581.

## Acknowledgements

We thank the joint programme of CRDF and Russian Ministry of Education (Grants # REC-007, BRHE 2004 # Y2-C-07-02) and the Russian Foundation for Basic Research (Grants # 03-03-32372-a, 03-03-96225-r2003tatarstan_a) for financial support.

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