Syntheses and X-Ray Crystal Structures of New Copper(I) and Silver(I) Complexes containing Thione Ligands

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Received September 18th, 2000.

Dedicated to Professor Kurt Dehnicke on the Occasion of his 70th Birthday

Abstract. The reaction of $[(Ph_3P)_2CuCl]_2$ with 4-amino-6-methyl-1,2,4-triazine-thione-5-one (AMTTO, **1**) in methanol and further recrystallization from methanol/acetone solution gives $[(C_4H_4N_3SON(=CMe_2)Cu(PPh_3)_2Cl]$ (**2**) as a neutral complex.

$[(C_4H_4N_3SON(=CMe_2)Ag(PPh_3)_2]NO_3$ (**4**) can be obtained in excellent yield by the reaction of $[(AMTTO)_2Ag]NO_3$ (**3**) with triphenylphosphane in methanol/acetone. Both complexes were characterized by infrared spectroscopy, elemental analyses as well as by X-ray diffraction studies. Crystal data for **2** at –80 °C: space group $P\bar{1}$ with a = 1233.8(1), b = 1389.7(1), c = 1417.1(1) pm, α = 89.36(1)°; β = 65.10(1)°, γ = 65.95(1)°, Z = 2, R_1 = 0.0582 and for **4** at –80 °C: space group $P\bar{1}$, with a = 1193.3(1), b = 1308.5(1), c = 1385.3(1) pm, α = 94.69(1)°, β = 109.14(1)°, γ = 93.42(1)°, Z = 2, R_1 = 0.0716.

Keywords: Triazine; Copper; Silver; Crystal structures

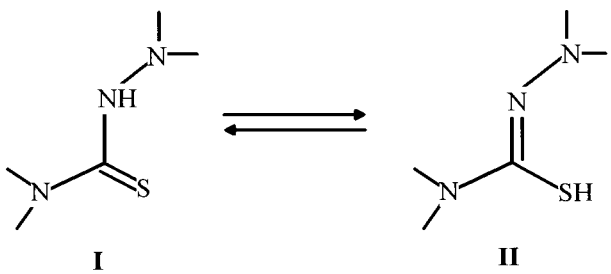
Synthesen und Kristallstrukturen neuer Kupfer(I)- und Silber(I)-Komplexe mit Thion-Liganden

Inhaltsübersicht. Die Reaktion von $[(Ph_3P)_2CuCl]_2$ mit 4-Amino-6-methyl-1,2,4-triazin-thion-5-on (AMTTO, **1**) in Methanol sowie Umkristallisation aus Methanol/Aceton ergibt den Neutralkomplex $[(C_4H_4N_3SON(=CMe_2)Cu(PPh_3)_2Cl]$ (**2**).

$[(C_4H_4N_3SON(=CMe_2)Ag(PPh_3)_2]NO_3$ (**4**) kann in sehr guter Ausbeute erhalten werden, wenn $[(AMTTO)_2Ag]NO_3$ (**3**) mit Triphenylphosphan in Methanol/Aceton umgesetzt wird. Die Komplexe wurden mittels IR-Spektroskopie, Elementaranalysen und Röntgenstrukturanalysen charakterisiert. Kristalldaten für **2** bei –80 °C: Raumgruppe $P\bar{1}$ mit a = 1233,8(1), b = 1389,7(1), c = 1417,1(1) pm, α = 89,36(1)°; β = 65,10(1)°, γ = 65,95(1)°, Z = 2, R_1 = 0,0582 und für **4** bei –80 °C: Raumgruppe $P\bar{1}$, mit a = 1193,3(1), b = 1308,5(1), c = 1385,3(1) pm, α = 94,69(1)°, β = 109,14(1)°, γ = 93,42(1)°, Z = 2, R_1 = 0,0716.

1 Introduction

The ligand 4-amino-6-methyl-1,2,4-triazine-thione-5-one ($C_4H_4N_3SONH_2$, AMTTO, **1**), which contains the –N(H)–C(=S)– chromophore exists in two tautomeric forms **I** and **II** (scheme I).



I **II**

Scheme 1 Tautomeric forms in thiosemicarbazides and thiosemicarbazones.

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Consequently, there has been considerable interest in the coordination properties of both the neutral thione **I** and of the deprotonated thiol **II** ligand [1, 2]. Crystallographic investigations have shown that the thione **I** coordinates exclusively *via* the S atom [3]. In contrast, the thiolate of **II** can adopt a variety of coordination modes, namely: (i) S unidendate [2]; (ii) S,N-chelating [2, 3c, 4]; (iii) S,N-bridging [3c, 5] and (iv) S unidentate (with a weak M···N interaction) [6].

In our investigations we have shown that the AMTTO reacts with palladium(II) halides such as chloride, bromide or iodide as a S,N-chelating ligand [7] and with silver(I) nitrate according to the "Pearson Principle" [8] as a unidentate one *via* its sulphur atom with a weak Ag···N interaction, which leads to a 2 + 2 coordination on the silver atom [9].

As part of our continuing interest in the sythesis and characterization of heterocyclic thione complexes of transition metals, we wish to report on further thione metallacycles containing copper(I) and silver(I) ions.

2 Syntheses and Characterization of 2 and 4

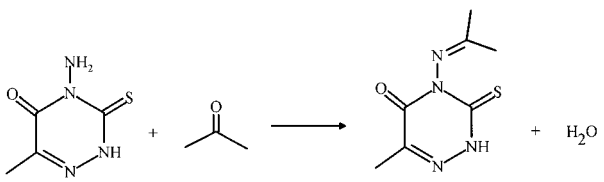
2 can be obtained by the reaction of CuCl, PPh_3 and **1** in a molar ratio 1:2:1 in methanol at 50 °C and further recrystallization of the crude from acetone solution at room temperature according to equation (1).

$$CuCl + 2\,PPh_3 + C_4H_4N_3SONH_2 \xrightarrow[-H_2O]{MeOH/Me_2CO} \underset{\mathbf{2}}{[(C_4H_4N_3SON(=CMe_2)Cu(PPh_3)_2Cl]} \quad (1)$$

4 can be prepared by the reaction of $[(AMTTO)_2Ag]NO_3$ (**3**) with PPh_3 in the molar ratio 1:1 in methanol/acetone [eq. (2)].

$$\mathbf{3} + 2\,PPh_3 \xrightarrow[-H_2O]{MeOH/Me_2CO} \underset{\mathbf{4}}{[(C_4H_4N_3SON(=CMe_2)Ag(PPh_3)_2]NO_3} + \mathbf{1} \quad (2)$$

In both complexes **2** and **4**, the NH_2-group of the ligand reacts with the solvent acetone in a Schiff's base reaction to the corresponding imine $C_4H_4N_3SON(=CMe_2)$ according equation (3).



(3)

2 is a yellowish crystalline solid and **4** is a colorless one. The absorptions *ν*CuS and *ν*CuCl of complex **2** can be observed at 305 and 208 cm^{-1}. In the IR spectra of **4** a broad band at 286 cm^{-1} can be assigned to *ν*AgN and *ν*AgS [10]. The C=O and C=N functions cause two vibrations at 1699 and 1614 cm^{-1} for **2** and 1700 and 1614 cm^{-1} for **4**, respectively. P–C vibrations of the moiety PPh_3 are found in the range 750–697 cm^{-1} for **2** and at 761–696 cm^{-1} for **4**. The NO_3^- anion presents its N–O asymmetric streching mode (E′) at 1377 cm^{-1} and the out-of-plane absorption (A_2'') at 826 cm^{-1}. For the N–H streching vibrations two broad weak absorptions could be found at 3442 (**2**) and 3439 (**4**) cm^{-1}, a result of the hydrogen bonding.

3 Results and Discussion

2 consists of a neutral molecule (Fig. 1), while **4** is a ionic compound which consists of the cation $[(C_4H_4N_3SON(=CMe_2)Ag(PPh_3)_2]^+$ and the anion NO_3^- (Fig. 2). The molecules and ions of **2** and **4** possess only C_1-symmetry. The coordination around the metal is distorted tetrahedral with two P atoms of the phosphane molecules, one S atom of the thione and one Cl atom. This arrangement is considerable distorted since the P angle at the metal site, P1–Cu1–P2 with a value of 126.62(5)°, is close to trigonally coordinated Cu(I), while three other selected angles in the CuP_2SCl group with 106.09(5)° (Cl1–Cu1–S1), 105.35(6)° (Cl1–Cu1–P1) and 103.00(6)° (P2–Cu1–S1) are nearly to those of a regular tetrahedron. The tetrahedral distortion is due to steric imposion of the bulky phosphane ligands and was observed in a series of analogous complexes [11]. The Cu–P bond distances, mean 229.2 pm, are within the range of the corresponding distances reported for other copper(I) complexes (227.7–230.7 pm) [12]. Similar Cu–Cl distances, here 238.0(1) pm, has been observed in four coordinated Cu(I) complexes (233.3–239.1 pm) [13].

The nitrogen-bound hydrogen atom in **2** participates in an intramolecular hydrogen bridge with the metal-bound chlorine atom; as illustrated in Fig. 1, this results in the formation of a CuClHNCS six-membered ring. The non-bonding distance N4···Cl1 of 304.7(5) pm indicates a strong hydrogen bridge (angle: N4–H1···Cl1 169(5)°). The Cu–S distance of 237.8(1) pm is consistent with the distances usually found for tetrahedrally coordinated copper(I) ions with thione-S donors [13, 14].

In the cation of **4** the ligand chelates the silver atom through its sulphur and iminic nitrogen atom (Fig. 2) forming a five-membered ring. Two PPh_3 molecules are also bound to the central atom and complete the distorted tetrahedral coordination around the silver atom. The deviation from perfect tetrahedral coordination is best illustrated by the P1–Ag1–P2 angle of 124.33(6)° and can be accounted for the steric hindrance induced by the two phosphane molecules, consequently compressing the S1–Ag1–N2 angle to 70.6(1)°.

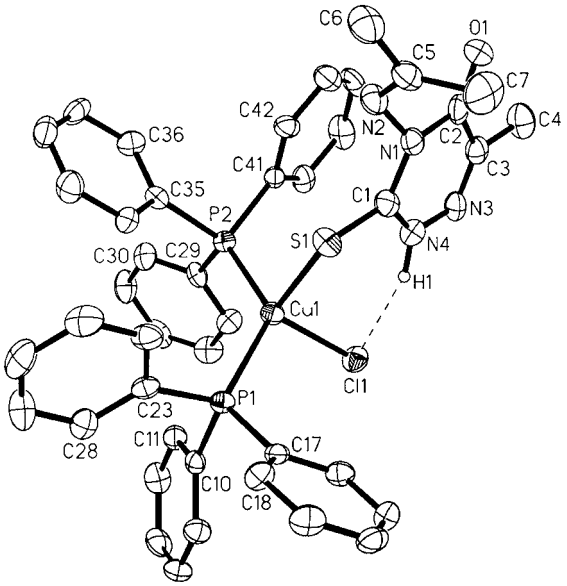


Fig. 1 Molecular structure of **2** (only H1 is shown; 50% probability level).

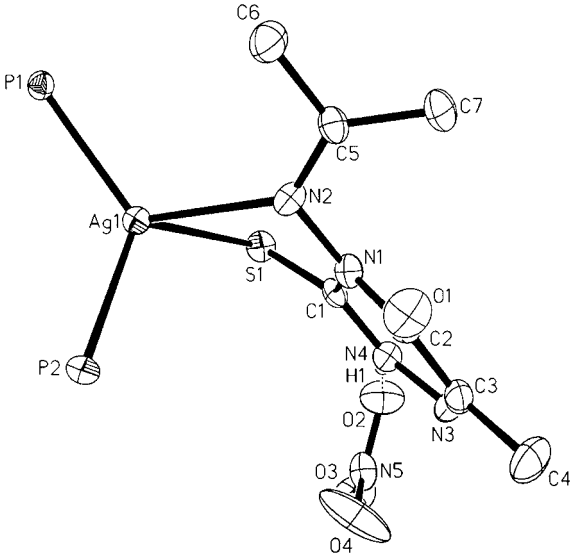


Fig. 3 View on the envelope comformation of the central metallacycle in **4** (without phenyl rings).

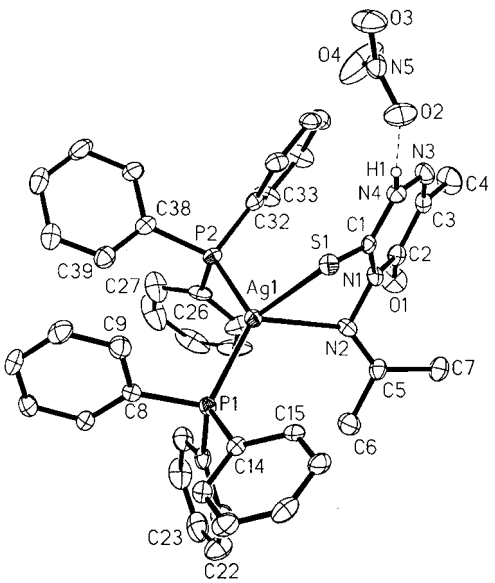


Fig. 2 Structure of the ion pair **4** (only H1 is shown).

The existance of a medium strong hydrogen bond between the NH-group of the ligand and an oxygen atom of the nitrate anion [N4 $\cdots$ O2: 275.7(7) pm] also contributes to the angular distortion about the silver atom. In contrast to **3**, where the ligand bound in a 1 + 1 fashion (strong Ag–S bond; weak and long Ag $\cdots$ N contact) to Ag^+ [9], in **4** the ligand acts more bidentately. This may be caused by the existance of the iminic group although there should be no back-bonding effects from Ag^+ to the imin function, which are important for classical d-block ions such as Fe^{III} or Mn^{III}. However, the Ag–N distance of 245.9(6) pm indicates still a long and relatively weak but significantly shorter bond than the 250.4(3) pm in **3**. 224 pm are generally accepted as typical Ag–N distance [15] but Ag1–N2 is clearly shorter than the sum of van der Waals radii of silver and nitrogen (155 + 170 = 325 pm) [16].

The Ag–P bond distances, 243.0(2) (Ag1–P1) and 249.0(2) pm (Ag1–P2), agree well with the values 242.6–250.4 pm measured for a number of complexes containing silver atoms coordinated by two Phosphanes [17]. The Ag–S bond lengths of 262.9(2) is significantly longer than the distance found in **3** [243.50(8) pm], where a 2 + 2 coordination around the Ag^+ center was observed. Although, the value of **4** lies in the range which was found for Ag^I complexes with coordination number four [18]. The hydrogen bridge causes sligthly different N–O bond lenghts within the standard deviations in the strictly planar nitrate ion. So, the distance O2–N5 (127.2(8) pm) including the oxygen which participates in the H bridge is somewhat longer than the other two N–O bonds (O3–N5: 125.6(8) pm; O4–N5: 118.5(9) pm), whereas the bond angles are very close to the ideal value of 120°.

The distances C5=N2 of 127.2(6) pm for **2** and of 127.9(9) pm for **4** are characteristic for acetone thiosemicarbazones (C=N: 126.6(7) pm) and acetone semicarbazone (C=N: 127.8 pm). The similar C–C bond lengths and C–C–C bond angles of the imine groups for **2** (C5–C6: 149.2(7); C5–C7: 149.3(8); C6–C5–C7: 117.5(5)°) and **4** (C5–C6: 150(1); C5–C7: 150(1); C6–C5–C7: 117.5(7)°) were measured in acetone thiosemicarbazone (C–C: 149.1(8), 148.6(7); C–C–C: 117.4(5)) and in acetone semicarbazone (C–C: 149.4, 149.9 pm; C–C–C: 125.0°) [19]. There is no π-electron conjugation between the AMTTO skeleton and the imin function in **2** and **4**. The dihedral angle between

the AMTTO plane and the plane N2/C5/C6/C7 amounts to 69° in **2** and to 59° in **4**. The central metallacycle AgN_2CS in **4** possess a envelope conformation with an angle of 48° enlosed by the planes Ag1/S1/N2 and S1/C1/N1/N2 (Fig. 3).

4 Experimental Section

The following chemicals were purchased and used without further purification: CuCl, $AgNO_3$, MeOH, Me_2CO (Merck) and PPh_3 (Fluka). **1** was prepared according to literature procedures [20]. The IR spectra were obtained on a Bruker IFS-88 (nujol mulls; CsI disks of the range 4000–500 cm^{-1}; polyethylen disks for the range 500–100 cm^{-1}).

$[(C_4H_4N_3SON(=CMe_2)Cu(PPh_3)_2Cl]$ (2). A solution of **1** (0.15 g, 1 mmol) in 10 mL of methanol was added dropwise to a solution of CuCl (0.09 g, 1 mmol) and Ph_3P (0.52 g, 2 mmol) in 20 mL of methanol and stirred for 3 h at 60–70 °C. The solvent was evapourated to a small volume (ca. 10 mL) to give a yellow solid which was dissolved by addition of 10 mL of acetone at room temperature. The solution was evapourated again to a small volume, the formed crude crystalline material was filtered off and the clear solution was kept at 4 °C to give yellowish crystals of **2**.

Yield: 0.71 g (87%).

Elemental analysis: $C_{43}H_{40}ClCuN_4OP_2S$ (821.83): calcd C 62.84, H 4.90, N 6.81, Cl 4.31, P 7.53, Cu 7.73, S 3.90; found C 62.77, H 4.91, N 6.93, Cl 4.20, P 7.33, Cu 7.62, S 3.84%.

IR (Nujol; cm^{-1}): 3442 w (νNH, br), 2757 w, 1729 vw, 1699 s (νC=O), 1614 m (νN=C, imine), 1516 s (νN=C, triazine), 1443 s, 1283 s, 1185 vw, 1152 w, 1092 m, 1077 vw, 1023 w, 1000 vw, 913 w, 847 m, 750 s (νPPh_3), 742 w (νPPh_3), 697 s (νPPh_3), 571 w, 510 m, 500 m, 441 m, 417 m, 345 w (br), 305 w (νCuS), 260 w, 208 m (νCuCl), 149 m (νCuP_2).

$[(C_4H_4N_3SON(=CMe_2)Ag(PPh_3)_2]NO_3$ (4). A solution of Ph_3P (0.52 g, 2 mmol) in 20 mL of methanol was added to a solution of **3** (0.48 g, 1 mmol) in 20 mL methanol/acetone (1 : 1) and stirred for 2 h at 70–80 °C. The solvent was evapourated to a small volume (ca. 10 mL) to give a colorless solid. The crude product was filtered off and the clear solution was kept at room temperature to give colorless crystals of **4**.

Yield: 0.81 g (91%).

Elemental analysis: $C_{43}H_{40}AgN_5O_4P_2S$ (892.70): calcd C 57.85, H 4.03, N 7.84, P 6.93, Ag 12.08, S 3.59; found C 57.21, H 4.03, N 8.09, P 6.71, Ag 11.98, S 3.34%.

IR (Nujol; cm^{-1}): 3439 vw (νNH, br), 2731 w, 1700 s (νC=O), 1614 m (νN=C, imine), 1527 m (νC=N, triazine), 1435 s, 1401 s, 1377 s (E′, νNO_3), 1298 s, 1250 s, 1196 m, 1174 m, 1152 m, 1098 s, 1073 m, 1043 w, 1030 m, 1000 m, 977 w, 935 w, 848 w, 825 w (A_2'', νNO_3), 815 w, 761 vs (νPPh_3), 750 vs (νPPh_3), 742 vs (νPPh_3), 695 vs (νPPh_3), 636 vw, 618 vw, 588 vw, 576 m, 516 s, 501 s, 498 s, 394 m (br), 286 m (br, νAgN, νAgS), 144 s (νAgP_2).

*Crystal structure analyses of **2** and **4***

The crystals of **2** and **4** were covered with a perfluorinated polyether and mounted on the top of a glass capillary under a flow of cold gaseous nitrogen. The orientation matrix and preliminary unit cell dimensions were determined from 15 (CAD4, Enraf-Nonius) reflections (graphite-monochromated MoKα radiation; $\lambda = 71.073$ pm). The final cell parameters were determined from 25 reflections. The intensities were corrected for Lorentz and polarization effects. In addition

Table 1 Crystallographic data for **2** and **4**

Compound	**2**	**4**
Formula	$C_{43}H_{40}ClCuN_4OP_2S$	$C_{43}H_{40}AgN_5O_4P_2S$
Formula weight/gmol^{-1}	821.83	892.70
Crystal size/mm	0.41×0.38×0.12	0.39×0.32×0.15
a/pm	1233.8(1)	1193.3(1)
b/pm	1389.7(1)	1308.5(1)
c/pm	1417.1(1)	1385.3(1)
α/°	89.36(1)	94.69(1)
β/°	65.10(1)	109.14(1)
γ/°	65.95(1)	93.42(1)
Volume/10^6 pm^3	1974.5(3)	2028.0(3)
Z	2	2
ρ/gcm^{-3}	1.382	1.462
Temperature/K	193	193
μ/cm^{-1}	7.9	6.8
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
No. [26]	2	2
2θ-range/°	5.8–55.8	4.6–50.0
h	–13 ≤ 0	–14 ≤ 13
k	–16 ≤ 14	–15 ≤ 15
l	–15 ≤ 15	0 ≤ 16
No. of reflections	7038	7623
Unique reflections (R_{int})	5574 (0.0477)	7120 (0.0474)
Reflections with $F_o > 4\sigma(F_o)$ for R_1	4225	5221
Parameters	483	509
R_1	0.0582	0.0716
wR_2 (all Data)	0.1545[a]	0.2134[b]
Max./min. residual electron density/e · pm^{-3} · 10^{-6}	0.57/–0.78	1.38/–1.74

[a] $w = 1/[\sigma^2(F_o^2) + (0{,}0954 \cdot P)^2]$; $P = [\max(F_o^2, 0) + 2 \cdot F_c^2]/3$.
[b] $w = 1/[\sigma^2(F_o^2) + (0{,}1522 \cdot P)^2]$.

Table 2 Selected bond lengths/pm and angles/° of **2** and **4**[a]

2

Cu1–Cl1	238.0(1)	Cl1–Cu1–S1	106.09(5)	Cu1–S1–C1	106.5(2)
Cu1–S1	237.8(1)	Cl1–Cu1–P1	105.35(6)	S1–C1–N1	123.7(4)
Cu1–P1	227.7(1)	Cl1–Cu1–P2	104.89(5)	N1–N2–C5	115.3(4)
Cu1–P2	230.7(1)	S1–Cu1–P1	109.35(5)	C6–C5–C7	117.5(5)
S1–C1	167.7(5)	S1–Cu1–P2	103.00(6)	N2–N1–C1	115.3(4)
C1–N1	135.3(6)	P1–Cu1–P2	126.62(5)	N2–N1–C2	118.0(5)
N1–N2	143.5(6)			C1–N1–C2	124.0(4)
N2–C5	127.2(6)				
C5–C6	149.2(7)				
C5–C7	149.3(8)				

4

Ag1–S1	262.9(2)	S1–Ag1–P1	118.24(6)	Ag1–S1–C1	95.0(2)
Ag1–P1	243.0(2)	S1–Ag1–P2	112.64(6)	Ag1–N2–N1	109.1(4)
Ag1–P2	249.0(2)	P1–Ag1–P2	124.33(6)	N1–N2–C5	115.1(5)
Ag1–N2	245.9(6)	S1–Ag1–N2	70.6(1)	N2–C5–C6	115.4(6)
S1–C1	167.3(7)	P1–Ag1–N2	116.9(2)	N2–C5–C7	127.1(7)
C1–N1	137.9(9)	P2–Ag1–N2	99.6(2)	C6–C5–C7	117.5(7)
N1–N2	141.9(7)			O2–N5–O3	118.6(7)
N2–C5	127.9(9)			O2–N5–O4	119.7(7)
C5–C6	150(1)			O3–N5–O4	121.6(8)
C5–C7	150(1)			N2–N1–C1	116.1(5)
O2–N5	127.2(8)			N2–N1–C2	119.3(5)
O3–N5	125.6(8)			C1–N1–C2	123.5(6)
O4–N5	118.5(9)				

[a] Further details can be obtained from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ by quoting the numbers CCDC 158749 (**2**) and 158750 (**4**) (Fax: (+44)12 23-3 36-0 33; e-mail: deposit@ccdc.cam.ac.uk).

absorption corrections were performed in both cases (empirical, 10 φ-scans, for further details see Table 1). The structures were solved by direct methods for **2** (SHELXTL [23]) and by the Patterson method for **4** (SHELXTL-Plus [21]) and refined against F^2 by full-matrix least-squares using the program SHELXL-97 [22]. The N–H hydrogen atoms in both complexes are freely refined. The C–H hydrogen atoms were calculated for ideal positions and refined with a common displacement parameter. Used programs were SHELXTL, SHELXTL-Plus, SHELXL-97, ORTEP [24] and PLATON-98 [25].

S. C. and *B. N.* thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

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