Coordinatively and Electronically Unsaturated Pentamethylcyclopentadienyliridium(III) Complexes with the Dianions of Biuret, of the Diamide of Malonic Acid and of an *N*-Acetyldipeptide Ester[‡]

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Dedicated to Professor Karl Wieghardt on the occasion of his 60th birthday

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The dianions of biuret, of the diamide of malonic acid and of *N*-acetyl-L-alanyl-L-alanine methyl ester give the coordinatively unsaturated 16-electron *N*,*N*′-chelate complexes [Cp*Ir[NHC(O)NHC(O)NH)] (**1**), [Cp*Ir[NHC(O)CH_2C(O)NH)] (**2**) and {Cp*Ir[N($COCH_3$)CH(CH_3)C(O)NCH(CH_3)CO_2Me]} (**3**) upon reaction with $[Cp^*IrCl_2]_2$. From $[(R_3P)PdCl_2]_2$ (R = Et, Ph) and biuret the complexes $[(Cl)(R_3P)Pd(\eta^2\text{-biureto})Pd]^-Na^+$ were obtained. The X-ray structure determinations of **1** and **3** reveal that the almost planar chelate rings lie perpendicular to the Cp* ring.

Introduction

The long and interesting history of biuret was reviewed by Kurzer in 1956.[2] The copper(II) complex of biuret was one of the first complexes of all,[3] and the biuret reaction, the formation of a red-violet copper compound with peptides was discovered even earlier in 1833.[4] Schiff[5] found later that the diamides of malonic acid and of oxalic acid form similar copper(II) complexes as with biuret, and the pioneers in coordination chemistry Tschugaeff[6] and Pfeiffer[7] proposed correct formulas for the biuret copper(II) chelate and analogous complexes, the structures of which were later confirmed by the X-ray diffraction studies of Freeman et al.[8]

Other chelate complexes with the dianion of biuret, including Cu^{III} and Ni^{III} complexes, have also been reported.[9] We thought it would be interesting to introduce the classical ligand biuret into organometallic chemistry. As shown below, the coordinatively unsaturated sixteen electron complexes Cp*Ir(L-L) **1**−**3** resulted from the reactions of the chloro-bridged complex $[Cp^*IrCl_2]_2$ with the dianions of biuret, its C analogue malodiamide and of an acetyldipeptide ester. Closely related to these new compounds are Grotjahn's Cp* complexes with the dianions of *N*-acyl and *N*-sulfonyl α-amino acids.[10] Other coordinatively unsaturated complexes are, for example, $[CpM(NO)R_2]$ and $[CpM(NO)L]$ (M = Mo, W),[11] $[CpMo(PR_3)_2Cl]$,[12] $[(arene)Ru(SR)_2]$,[13] [CpCo(1,2-ethylenedithiolato)],[14,15] $[Cp^*Ru(PR_3)OR]$,[16] $[Cp^*Ru(R_2NCH_2CH_2NR_2)]^+$,[17] $[M(CO)_3(O,S\text{-}C_6H_4)]^{2-}$ and $[(OC)_3MS_2C_6R_4]^{2-}$ (M = Cr, Mo, W).[18] Noyori's coordinatively unsaturated half-sandwich complex [(arene)RuNHCH(Ph)CH(Ph)-$NSO_2C_6H_4$Me] is an efficient catalyst for asymmetric hydrogen transfer to ketones.[19] The 16-electron complexes $[Cp^*M(L\text{-}L')]^+$ (M = Ru, Fe) with P,P- or P,O-donors have been studied by several groups as catalysts.[20] The geometry of coordinatively unsaturated two-legged piano-stool complexes with 16 valence electrons has been analysed theoretically.[21]

Results and Discussion

Reaction of the chloro-bridged iridium complex $[Cp^*IrCl_2]_2$ with biuret, malodiamide or *N*-acetyl-L-alanyl-L-alanine methyl ester in the presence of NaOMe gives the chelate complexes **1**−**3**.

The wine-red colour of these complexes is characteristic of 16-electron iridium complexes.[10] Addition of triphenylphosphane to **1** and **3** in methanol affords yellow solutions which show only one ^{31}P NMR signal (**1**: δ = 8.62 ppm; **3**: δ = 8.05 ppm) in the ^{31}P NMR spectra due to the corresponding 18-electron species.[10] The colour change from wine red to yellow can be explained by the π-donor function of the chelate ligands in the 16-electron complexes.[10,18]

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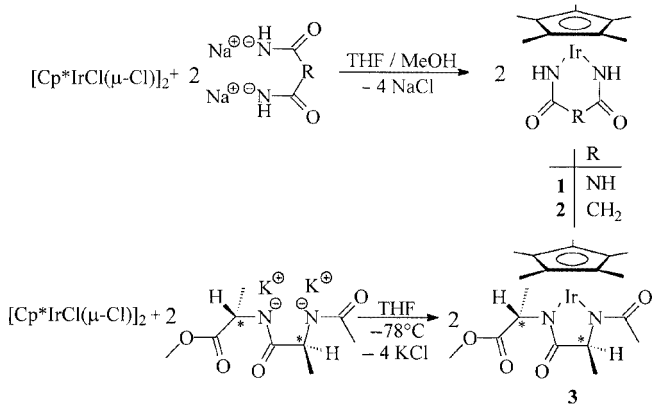


The IR, ^1H and ^{13}C NMR spectra of **1**–**3** exhibit the expected data (see Exp. Sect.). In the ^1H and ^{13}C NMR spectra of **3** only one set of signals is detected which shows that diastereoisomers of **3** were not formed. Complex **2** could not be obtained analytically pure. In the mass spectra of the product from malodiamide the ions of dimers $\{Cp_2^*\text{-}Ir_2Cl_2[NHC(O)CH_2C(O)NH)]\}^+$ (*m/z* = 826; 6%), $\{Cp_2^*\text{-}Ir_2Cl[NHC(O)CH_2C(O)NH]\}^+$ (*m/z* = 789; 4%) and $\{Cp_2^*\text{-}Ir_2[NHC(O)CH_2C(O)NH]\}^{2+}$ (*m/z* = 378; 3%) were observed.

The X-ray structure analysis of **1** (Figure 1) and **3** (Figure 2) reveals the typical geometry of a two-legged pianostool half-sandwich complex, due to the coordinatively unsaturated nature of these compounds. Although water molecules were found in the unit cells of both compounds they definitely do not coordinate because of the large distance to the iridium atoms (**1**: ≥439.8 pm, **3**: 600.7 pm). The planes formed by the Cp* ligands in **1** and **3** are almost perpendicular (**1**: 91.8°; **3**: 93.3°) to the planes formed by the two coordinating nitrogen atoms and the two carbon atoms connected to them. This has also been found in other 16-electron half sandwich complexes with chelate ligands.[10,14,19] Of great interest are the observed bond lengths for the Ir–N bonds. In compound **1** those bond lengths are 195.1(8) pm [Ir(1)–N(1)] and 197.8(6) pm [Ir(1)–N(3)]. In compound **3** these bond lengths were found to be 198.3(2) pm [Ir(1)–N(2)] and 201.3(6) pm [Ir(1)–N(1)]. A comparison with the Ir–N bond lengths (ca. 210 pm) in 18-electron complexes with monosubstituted deprotonated amide ligands,[22] for example in [Cp*(Cl)Ir(Leu-LeuOMe-H$^+$)][23] shows a significant shortening of the Ir–N bond in compounds **1** and **3**. This decrease in the Ir–N bond length is in good agreement with the decline observed by Grotjahn and Noyori in their 16-electron half-sandwich chelate complexes.[10,14] The most reasonable explanation for this bond shortening is that besides the usual σ-symmetrical interaction of a filled ligand orbital with an empty metal orbital (σ-donation), an additional π-symmetrical interaction of another filled orbital of the anionic heteroatom ligand with an empty metal orbital of suitable symmetry (π-donation) is present.[10,18] The contribution of lone-pair electrons at the anionic heteratom ligand to the π-donation explains the exceptional stability of these compounds; the dark red colour results from LMCT in those compounds. The C–N bond lengths in **1** are 2–3 pm longer than in "free" biuret.[24]

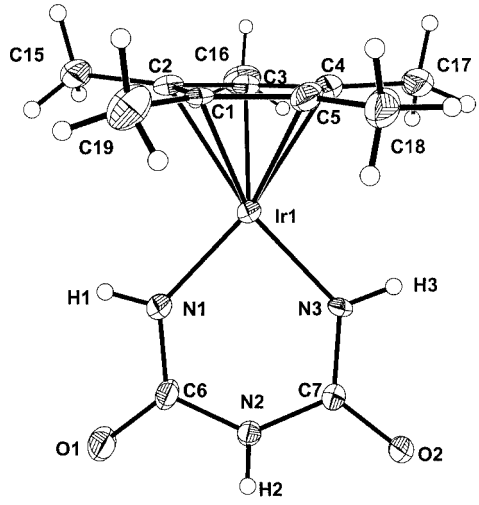


Figure 1. Molecular structure of **1** in the crystal

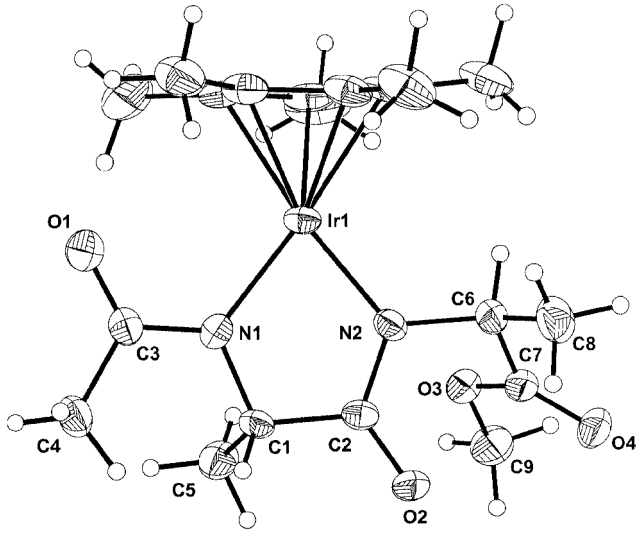
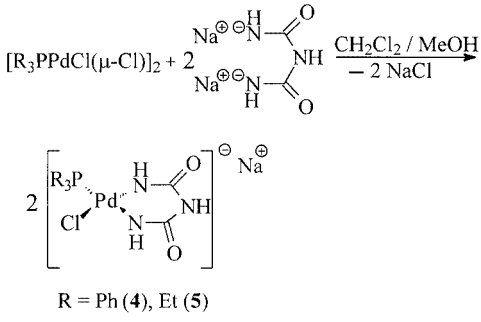


Figure 2. Molecular structure of **3** in the crystal

The chloro-bridged palladium(II) complexes $Pt_2(PR_3)_2Cl_4$ afforded the yellow anionic chelates **4** and **5** with the biuret dianion. They were characterised by their IR and NMR spectroscopic data (see Exp. Sect.). As for **1** and **2** the NH signals of CD_3OD solutions of **4** and **5** cannot be observed in the ^1H NMR spectra because of a rapid H/D exchange. The ^{31}P NMR spectra of **4** and **5** exhibit only one signal.



Experimental Section

The chloro-bridged complexes $[Cp^*IrCl_2]_2$ [25] and $[PdCl_2(PR_3)]_2$ [26] were obtained according to literature procedures. All reactions were carried out in Schlenk tubes under argon.

Cp*(η²-*N*,*N*-biureto)Ir^{III} (1): A solution of biuret (41.2 mg, 0.4 mmol) and 0.4 mmol of NaOMe in 10 mL of methanol was added dropwise to a suspension of $[Cp^*IrCl_2]_2$ (159.3 mg, 0.2 mmol) in 15 mL of methanol whilst stirring at room temperature. The solution turned dark red and was then stirred for 48 h. The solvent was then removed in vacuo. NaCl could not be separated from the product by chromatography. The dark red product was dried at 75 °C for 4 days. Yield 65 mg (77%). IR (KBr): $\tilde{\nu}$ = 3403 cm^{-1} s (NH sec. amide), 3294 s (NH prim. amide), 1650 vs (CO, amide I), 1635 m (NH-bending, amide II). ^{1}H NMR (270 MHz, CD_3OD): δ = 1.85 (s, 15 H, Cp*) ppm. ^{13}C NMR (67.9 MHz, CD_3OD): δ = 8.2 (s, Cp*), 88.7 (s, Cp*), 163.1 (s, CO) ppm. $C_{12}H_{18}IrN_3O_2$·2.25NaCl (559.98): calcd. C 25.74, H 3.24, N 7.50; found C 25.57, H 3.16, N 7.83.

Cp*(η²-*N*,*N*-malodiamine-2H$^+$)Ir^{III} (2): $[Cp^*IrCl_2]_2$ (159.3 mg, 0.2 mmol) in 15 mL of THF was added to a solution of malodiamide (40.8 mg, 0.4 mmol) and NaOMe (0.8 mmol) in 10 mL of methanol whilst stirring at room temperature. The solution became wine red. After stirring for 16 h at room temperature the solvent was removed in vacuo. Complex **2** was not analytically pure. Efforts to purify the compound by recrystallization from methanol led to decomposition. IR (KBr): $\tilde{\nu}$ = 3295 cm^{-1} s (NH), 2984 s (CH), 2944 s (CH), 2685 s, 2625 s, 2606 s ($HNEt_3^+$), 1676 vs (CO, amide I), 1620 m (NH-bending, amide II), 1586 w ($HNEt_3^+$), 1398 m (CH), 1384 m (CH). ^{1}H NMR (400.1 MHz, CD_3OD): δ = 1.61 (s, 15 H, Cp*), 3.35 (m, 2 H, CH_2) ppm. ^{13}C NMR (100.5 MHz, CD_3OD): δ = 5.8 (s, Cp*), 52.9 (s, CH_2), 85.2 (s, Cp*), 169.7 (s, CO, malodiamide) 178.3 (s, CO). FAB$^+$MS (*m*-NBA): *m*/*z* (%) = 429 (86) [M + H], 329 (52) [M − ligand].

Cp*(η²-*N*-acetyl-L-alanyl-L-alanine methyl ester-2H$^+$)Ir^{III} (3): [Cp*$IrCl_2]_2$ (159.3 mg, 0.2 mmol) in 15 mL of THF was stirred for 2 h at −78 °C (2-propanol/dry ice) and to this mixture was added a suspension of *N*-acetyl-L-Ala-L-Ala-OMe (86.5 mg, 0.4 mmol) and K_2CO_3 (165.8 mg, 1.2 mmol) in 15 mL of cold THF. The reaction mixture was allowed to warm to room temperature for 18 h and an almost clear wine-red suspension was formed. The solvent was then removed in vacuo and the residue treated with 15 mL of dichloromethane and stirred for 30 min. KCl and excess K_2CO_3 were centrifuged off and the solution concentrated to dryness to give a dark red microcrystalline product. Yield 88 mg (82%). IR (KBr): $\tilde{\nu}$ = 2924 cm^{-1} s (CH), 2851 s (−O-CH_3), 1738 vs (COOMe), 1630 s (CO amide I), 1375 s (−CO-CH_3). ^{1}H NMR (270 MHz, CD_2Cl_2): δ = 1.33 (d, $^3J_{H,H}$ = 10.27 Hz, 3 H, α-CH_3), 1.35 (d, $^3J_{H,H}$ = 9.99 Hz, 3 H, α-CH_3), 1.76 (s, 15 H, Cp*), 1.95 (s, 3 H, Ac-N), 3.70 (s, 3 H, Me-O), 4.50 (m, 2 H, α-H) ppm. ^{13}C NMR (67.9 MHz, CD_2Cl_2): δ = 9.9 (s, Cp*), 22.9 (s, β-C), 23.2 (s, β-C), 30.2 (s, $NCOCH_3$), 51.5 (s, $COOCH_3$), 61.4 (s, α-C), 62.6 (s, α-C), 88.9 (s, Cp*), 173.7 (s, $NCOCH_3$), 174.0 (s, $COOCH_3$), 190.5 [s, N-CO-$C(CH_3)$N] ppm. The analysed substance was recrystallised from methanol. $C_{19}H_{29}IrN_2O_4$·MeOH (573.69): calcd. C 41.87, H 5.80, N 4.88; found C 41.56, H 5.97, N 4.89.

[Cl(Ph$_3$P)(η²-biureto)Pd]$^-$Na$^+$ (4): A solution of biuret (41.2 mg, 0.4 mmol) and NaOMe (0.8 mmol) in 10 mL of methanol was added to $[(Ph_3P)PdCl_2]_2$ (176 mg, 0.2 mmol) in 10 mL of methanol whilst stirring at room temperature. After 1 h the solution turned yellow and was stirred for another 17 h at room temperature. The solvent was then removed in vacuo. The residue was treated with 15 mL of methanol, filtered over celite and the solvent was again removed in vacuo. The yellow product was washed with 10 mL of hexane , centrifuged and dried at 60 °C in vacuo for two days. IR (KBr): $\tilde{\nu}$ = 3373 cm^{-1} s (NH sec. amide), 3234 m (prim. amide), 1630 vs (CO amide I), 1601 m (NH-bending amide II). IR (PE): $\tilde{\nu}$ = 378 cm^{-1} m (Pd-Cl). ^{1}H NMR (270 MHz, CD_3OD): δ = 7.78 (m, 15 H, Ph_3P) ppm. ^{31}P NMR (109.4 MHz, CD_3OD): δ = 27.99 (s, PPh_3) ppm. $C_{20}H_{18}ClN_3NaO_2PPd$ (528.2): calcd. C 45.48, H 3.43, N 7.96; found C 45.88, H 3.66, N 8.05. FAB-MS (*m*-NBA): *m*/*z* (%) = 506 (75) [M]$^-$, 471 (24) [M − Cl], 405 (5) [M − biuret], 244 (18) [M − P(Ph)$_3$].

[(Cl)(Et$_3$P)(η²-*N*,*N*-biureto)Pd]$^-$Na$^+$ (5): A solution of biuret (20.8 mg, 0.2 mmol) and NaOMe (0.4 mmol) in 10 mL of methanol was added to a solution of $[(Et_3P)PdCl_2]_2$ (59.1 mg, 0.1 mmol) in 10 mL dichloromethane whilst stirring at room temperature. The dark red mixture turned yellow. After stirring for 30 min the solvent was removed in vacuo and the residue dissolved in 15 mL of methanol and filtered over celite. The solvent was again removed in vacuo and the residue was treated with 20 mL of *n*-pentane and stirred for 10 min. The product was then separated by centrifugation and dried in vacuo. IR (KBr): $\tilde{\nu}$ = 3429 cm^{-1} s (NH sec. amide), 3201 m (NH prim. amide), 1630 vs (CO amide I), 1597 s (NH-bending amide II). IR (PE): $\tilde{\nu}$ = 360 cm^{-1} m (Pd-Cl). ^{1}H NMR (270 MHz, CD_3OD): δ = 1.21 [m, 9 H, P(CH_2CH_3)$_3$], 1.78 [m, 6 H, P(CH_2CH_3)$_3$] ppm. ^{31}P NMR (109.4 MHz, CD_3OD): δ = 24.56 (s, Et_3P) ppm. $C_8H_{18}ClN_3NaO_2PPd$·0.75NaCl (427.90): calcd. C 21.71, H 4.10, N 9.49; found C 21.26, H 4.53, N 9.53. FAB-MS (*m*-NBA): *m*/*z* (%) = 361 (55) [M]$^-$, 325 (17) [M − Cl], 244 (16) [M − PEt_3].

Crystal Structure Determination of 1 and 3: Suitable crystals of both compounds for the X-ray structure determination were obtained by slow evaporation of a methanolic solution. The data collection for compound **1** was done on a Siemens P4 four circle X-ray diffractometer with a Single Point detector at 293 K. Compound **3** was measured on a Stoe IPDS with an Image Plate detector at 200 K. The structure solution of **1** was done with the XS program from Bruker Analytical X-ray Systems (1997 Ver. 5.10) and the structure solution of **3** with the SHELXS-97 program (Sheldrick, 1990). Structure refinement for compound **1** was done with the SHELXTL suite of programs (Bruker Analytical X-ray Systems 1997 Ver. 5.10) and for the refinement of **3** the SHELXL-97 program (G. M. Sheldrick. University of Göttingen, 97−2 version) was used. For both structure determinations graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) was used. The hydrogen atoms H(1)−H(3) in compound **1** were found by difmap and refined freely. All other hydrogen atoms were inserted in idealised

Table 1. Selected experimentally observed bond lengths [pm] and angles [°] of **1**

Ir(1)−N(1)	195.1(8)	N(1)−Ir(1)−N(3)	86.5(3)
Ir(1)−N(3)	197.8(6)	C(6)−N(1)−Ir(1)	132.1(6)
N(1)−C(6)	132.9(1)	C(6)−N(2)−C(7)	130.2(7)
N(3)−C(7)	133.0(9)	N(2)−C(7)−N(3)	118.3(7)
O(1)−C(6)	124.5(1)	C(7)−N(3)−Ir(1)	132.1(5)
O(2)−C(7)	124.7(9)	O(1)−C(6)−N(1)	122.9(8)
N(2)−C(6)	136.5(1)	O(1)−C(6)−N(2)	117.0(8)
N(2)−C(7)	137.9(1)	O(2)−C(7)−N(2)	118.2(7)
		O(2)−C(7)−N(3)	123.5(7)

Table 2. Selected experimentally observed bond lengths [pm] and angles [°] of **3**

Ir(1)−N(1)	201.3(6)	N(1)−Ir(1)−N(2)	80.0(2)
Ir(1)−N(2)	198.3(2)	C(1)−N(1)−Ir(1)	115.7(4)
N(1)−C(1)	146.8(9)	N(1)−C(1)−C(2)	109.4(6)
C(1)−C(2)	149.5(1)	C(2)−N(2)−Ir(1)	118.6(5)
C(2)−N(2)	135.8(8)	Ir(1)−N(1)−C(3)	125.3(5)
O(1)−C(3)	121.3(1)	C(3)−N(1)−C(1)	119.0(6)
C(3)−N(1)	137.2(9)	Ir(1)−N(2)−C(6)	126.9(4)
N(2)−C(6)	148.5(9)	C(2)−N(2)−C(6)	114.2(6)
C(7)−O(4)	121.7(9)		
C(7)−O(3)	134.2(1)		
O(3)−C(9)	146.4(1)		

Table 3. Crystal data and structure refinements for compounds Cp*(η^2-*N*,*N*-biureto)Ir^{III} (**1**) and Cp*(η^2-*N*,*N*-[(*N*-acetyl)-L-alanyl-L-alanine-methyl ester)]Ir^{III} (**3**)

	1	**3**
Empirical formula	$C_{12}H_{18}IrN_3O_2$	$C_{19}H_{30}IrN_2O_4$
Formula weight	428.49	542.66
Temperature [K]	293(2)	200(2)
λ (Mo-K_α) [Å]	0.71073	0.7173
Crystal System	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
a [Å]	14.147(8)	8.7398(1)
b [Å]	14.333(2)	11.2680(2)
c [Å]	15.063(2)	21.8235(4)
α [°]	90.00	90.00
β [°]	95.87(2)	90.00
γ [°]	90.00	90.00
Volume [Å^3]	3038.2(19)	2149.180(60)
Z	4	4
$\rho_{calcd.}$ [Mg/m^3]	2.048	1.70190(5)
μ [mm^{-1}]	0.809	6.239
F(000)	1792	1084
Crystal size [mm]	0.40 × 0.25 × 0.25	0.25 × 0.24 × 0.11
2θ range [°]	3.76 to 50.12	4.06 to 54.94
Index ranges	$0 \le h \le 14$	$-28 \le h \le 28$
	$-14 \le k \le 14$	$-14 \le k \le 14$
	$-14 \le l \le 14$	$-11 \le l \le 11$
Reflections collected	9631	36359
Independent reflections	4768 [R_{int} = 0.0347]	4923 [R_{int} = 0.0581]
Observed reflections	4134 [$F > 2\sigma(F)$]	4469 [$F > 2\sigma(F)$]
Max. and min. transmission	0.910 and 0.715	0.5218 and 0.2774
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4768/0/371	4923/0/246
Goodness-of-fit on F^2	1.067	1.168
*R*1, *wR*2 [$I > 2\sigma(I)$]	0.0338, 0.0830	0.0345, 0.0795
*R*1, *wR*2 [all data]	0.0424, 0.0879	0.0453, 0.0828
Largest diff. peak and hole [e·Å^3]	1.351 and −1.584	1.348 and −2.328

positions and were refined riding on the atoms to which they are bonded. Compound **1** crystallises in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. Compound **3** crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell. The experimentally observed bond lengths and bond angles for **1** and **3** are compiled in Table 1 and Table 2. The crystallographic data and refinement details are summarized in Table 3. CCDC-180880 (**1**) and CCDC-181126 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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