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Four novel mononuclear and polynuclear Cu(I) thiosaccharinates with triphenylphosphane and bis(diphenylposphino)methane. Synthesis and structural study of $Cu_4(tsac)_4(PPh_3)_3$, $Cu(tsac)(PPh_3)_2$, $Cu_4(tsac)_4(dppm)_2$, and $Cu_2(tsac)_2(dppm)_2$

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ABSTRACT

Four new ternary complexes of copper(I) with thiosaccharin and phosphanes were prepared. The reaction of $[Cu_4(tsac)_4(CH_3CN)_2]$ (**1**) (tsac: thiosaccharinate anion) with PPh_3 in molar ratios Cu(I)/PPh_3 1:075 and 1:2 gave the complexes $[Cu_4(tsac)_4(PPh_3)_3] \cdot CH_3CN$ (**2**) and $Cu(tsac)(PPh_3)_2$ (**3**), respectively. The reaction of **1** with $Ph_2PCH_2PPh_2$ (dppm) in molar ratios Cu(I)/dppm 2:1 and 1:1 gave the complexes $[Cu_4(tsac)_4(dppm)_2] \cdot 2CH_2Cl_2$ (**4**) and $[Cu_2(tsac)_2(dppm)_2] \cdot CH_2Cl_2$ (**5**), respectively. All the compounds have been characterized by spectroscopic and X-ray crystallographic methods.

Complex **2** presents a tetra-nuclear arrangement with three metal centers in distorted tetrahedral S_2NP environments, the fourth one with the Cu(I) ion in a distorted trigonal S_2N coordination sphere, and the tsac anions acting as six electron donor ligands in μ_3-S_2N coordination forms. Complex **3** shows mononuclear molecular units with copper(I) in a distorted trigonal planar coordination sphere, built with the exocyclic S atom of a mono-coordinated thiosaccharinate anion and two P-atoms of triphenylphosphane molecules. With dppm as secondary ligand the structures of the complexes depends strongly on the stoicheometry of the preparation reaction. Complex **4** has a centrosymmetric structure. Two triply bridged $Cu_2(tsac)_2(dppm)$ units are joined together by the exocyclic S-atoms of two tsac anions acting effectively as bridging tridentate ligands. Complex **5** is conformed by asymmetric dinuclear moieties where the two dppm and one tsac ligands bridge two Cu(I) atoms and the second tsac anion binds one of the metal centers through its exocyclic S-atom.

1. Introduction

The heterocyclic thioamides (thiones) are systems of chemical and biological interest because they are good chelating agents for a great number of metal ions in different oxidation states [1–8]. They show tautomeric equilibrium in solution hence making them versatile complexing agents, especially for heavy metals [9]. Particular attention has been devoted in the last decades to the synthesis of copper complexes, in both the mono and divalent oxidation states, due to the great variety and flexibility of their coordination spheres [1c,10]. The relative stability of the Cu(I) and Cu(II) oxidation states depends on various factors such as the redox potentials of the ligands (L), the solubility of Cu(I)–L and Cu(II)–L adducts and the solvent polarity [10,11]. In particular thiolate compounds are good reducing agents for Cu(II), giving rise to little soluble Cu(I) complexes [8,10,12].

Among the studied ligands, the heterocyclic thioamides and its deprotonated counterparts, thioamidates (thionates) have attracted attention because the exocyclic sulfur and/or the endocyclic nitrogen atoms of the thioamido group may be involved in metal coordination, making then potentially mono- to poly-functional donor agents. These versatile S,N ligands are capable to bind metals in a great variety of coordination forms: N- or S-monodentate, N,S-chelate, and μ_2-S, μ_2-N,S, μ_3-N,S (η^2-S, η^1-N) or μ_4-N,S (η^3-S, η^1-N) bridges. As a consequence, a rich field of mononuclear, binuclear and complex poly-nuclear coordination compounds has developed. There are several reviews in the literature dealing with heterocyclic thioamide–metal coordination [1,10].

Ternary and quaternary Cu(I)-halide complexes with neutral thiones and mono- or diphosphanes have been extensively studied by several research groups [4,5,13]. In these complexes Cu(I)

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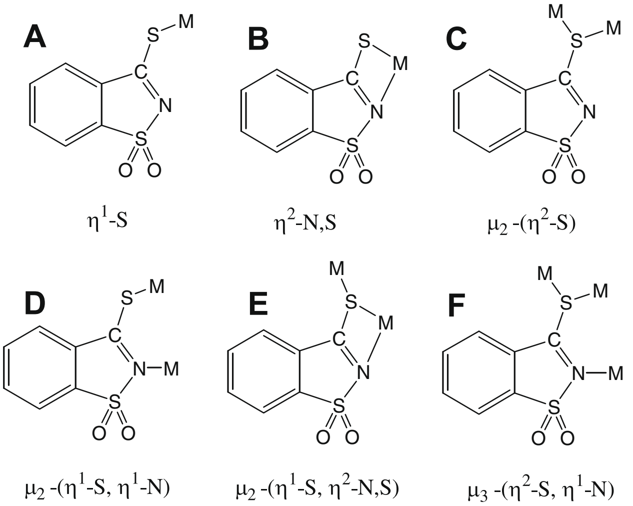
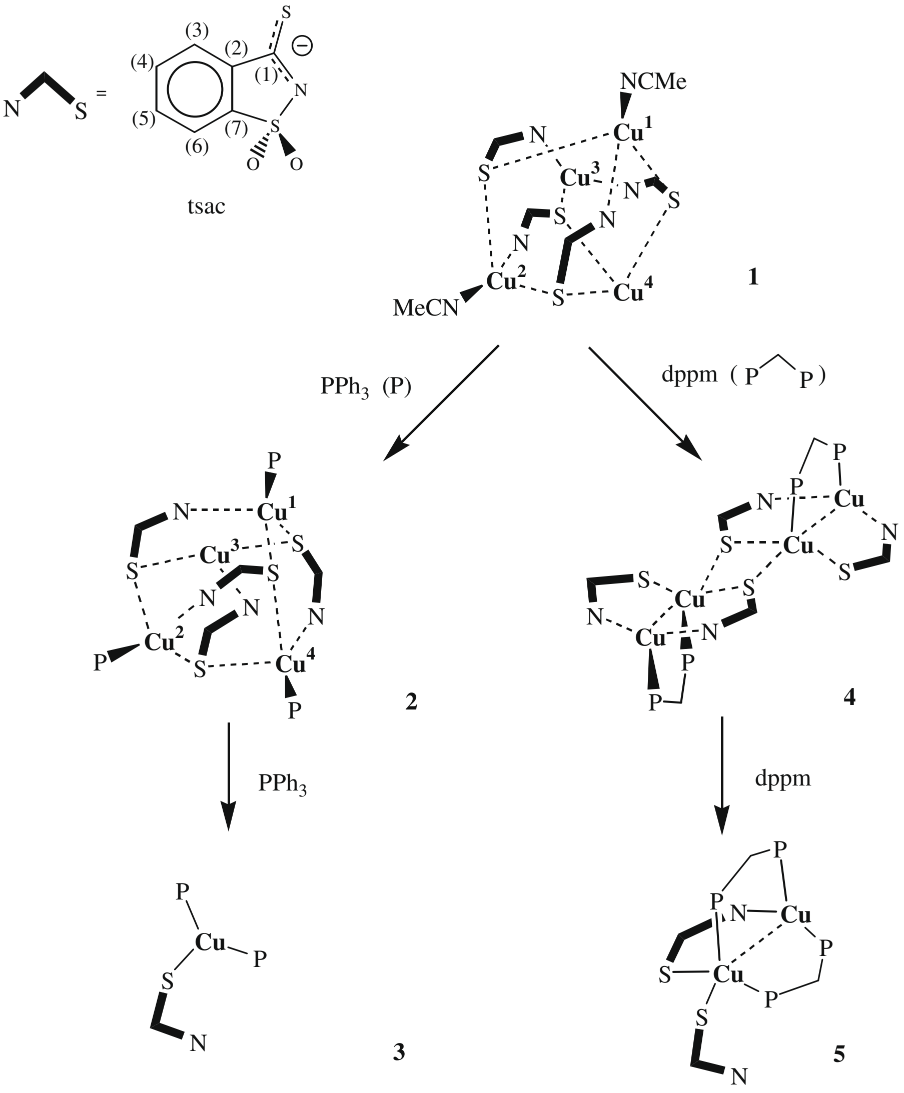
presents distorted trigonal or tetrahedral coordination spheres with the heterocyclic thiones bond to the metal as mono-dentate or bridging bi-dentate ligands through the thiocarbonilic sulfur atom (η^1-S and μ_2-S coordination forms, respectively). Among the chemistry of Cu(I) with thionates most of the research effort has been focused on the tetra-nuclear [6,14,15] or hexa-nuclear binary complexes [2,3,16] and also on the ternary Cu(I)–thioamidate–diphosphane complexes [7,17]. Copper–phosphane binding produces a large diversity of structural arrangements, with ligand to copper ratios from 1:1 to 4:2 [17,18]. Among them, the use of dppm as a bridging ligand between Cu(I) centers has developed a very rich structural chemistry of di-nuclear [19], tri-nuclear [20] and poly-nuclear [21] complexes.

Thiosaccharinate (1,2-benzoisothiazol-3-thionate-1,1-dioxide), the anion of thiosaccharin which is the thione form of saccharin, behaves as a versatile coordination agent for heavy metals. The anion has adopted a variety of coordination forms (Scheme 1) in the ternary metal thiosaccharinates with azines or phosphanes previously reported [22]. As part of a research to elucidate the coordination properties of metal thiosaccharinates, we present here the synthesis and the spectroscopic and X-ray diffraction study of four new Cu(I) complexes which exhibit different types of interaction between the thionate ligand and the metal centers: $[Cu_4(tsac)_4(PPh_3)_3]\cdot MeCN$, $[Cu(tsac)(PPh_3)_2]$, $[Cu_4(tsac)_4(dppm)_2]\cdot 2CH_2Cl_2$, and $[Cu_2(tsac)_2(dppm)_2]\cdot CH_2Cl_2$.



Scheme 1. Coordination forms of thiosaccharinate ligand.



Scheme 2. Copper thiosaccharinates obtained with increasing amounts of phosphanes.

2. Experimental

2.1. General remarks

All chemicals and solvents were of analytical reagent grade and used as purchased. Thiosaccharin in its solid α-form and $[Cu_4(tsac)_4(MeCN)_2] \cdot 2MeCN$ (**1**) were prepared following the techniques published previously [15]. The elemental composition analysis of C, H, and N were performed with a Carlo Erba EA1108 instrument at INQUIMAE (FCEyN, UBA, Argentina). The IR spectra in KBr pellets and Nujol mulls were recorded on a Nicolet Nexus FTIR spectrometer. The electronic spectra of solutions and solid spectra in BrK discs, were registered using a Cecil CE 2021 UV–Vis spectrophotometer. The ^1H, and $^{31}P\{^1H\}$ RMN spectra were recorded on a multinuclear Bruker ARX-300 equipment. The chemical shift data were measured by the replacement methods and are given relative to TMS and external H_3PO_4 (85%) standards. The numbering of the compounds can be seen above in Scheme 2. Conductivity measurements of acetonitrile (MeCN) solutions of compounds **2** and **3** were performed with an OAKTON digital conductimeter calibrated against aqueous solutions of twice re-crystallized KCl (744.7 ppm, 1413 μS).

2.2. Synthesis of the complexes

2.2.1. Tetrakis(thiosaccharinato)tris(triphenylphosphane)tetracopper(I) monoacetonitrile, $[Cu_4(tsac)_4(PPh_3)_3] \cdot MeCN$ (**2**)

Over a solution of complex **1** (0.010 g, 0.009 mmol) in acetonitrile (11 mL), a solution of PPh_3 (0.007 g, 0.03 mmol) in acetonitrile (10 mL) was slowly added with continuous stirring (Cu/PPh_3 molar ratio = 1/0.8). The final red solution was left to slowly evaporate at room temperature until half of its original volume was reached. The red single crystals obtained were filtered out, washed with diethyl ether and air dried. They showed light and air stability. Yield: 0.006 g (40%). *Anal. Calc.* for $C_{84}H_{64}Cu_4N_5O_8P_3S_8$: C, 53.8; H, 3.4; N, 3.7. Found: C, 54.2; H, 3.4; N, 3.6%. Molar conductance (Ω^{-1} mol^{-1} cm^{-1}): 33 (3.0×10^{-4} M solutions in MeCN). IR: (KBr, cm^{-1}): 3072w, 3053w, 1480m, 1461s, 1435s, 1399s, 1325s, 1236s, 1170vs, 1124s, 1095s, 1003s, 820m, 792m, 768m, 746m, 694s, 586m, 557s, 520m, 431m. ^1H NMR (DMSO-d^6, δ in ppm): δ 7.82–7.76 (m, 4H, H6); 7.72–7.65 (m, 4H, H3); 7.62–7.48 (m, 8H, H4/H5); 7.36–7.15 (m, 45 H, PPh_3); 2.05 (s, 3H, MeCN). $^{31}P\{^1H\}$ NMR (DMSO-d^6, δ in ppm): δ 53.22 (PPh_3).

2.2.2. Thiosaccharinato-bis(triphenylphosphane)copper(I), $[Cu(tsac)(PPh_3)_2]$ (**3**)

A solution of PPh_3 (0.042 g, 0,16 mmol) in acetonitrile (2 mL) was added to a red solution of copper thiosaccharinate (**1**) (0.024 g, 0,021 mmol) in acetonitrile (20 mL) under continuous stirring at room temperature (Cu/PPh_3 molar ratio = 1/2). A clear yellow solution was produced. After 4 days of slow evaporation of the solvent at room temperature, bright yellow crystals suitable for X-ray diffraction analysis were formed. The crystalline product was filtered out, washed with diethyl ether and dried in air. Yield: 0.043 g (68 %). *Anal.* Calc. for $C_{43}H_{34}CuNO_2P_2S_2$: C, 65.7; H, 4.4; N, 1.8. Found: C, 65.4; H, 4.7; N, 2.1%. Molar conductance (Ω^{-1} mol^{-1} cm^{-1}): 35 (1.0×10^{-3} M solutions in MeCN). IR (KBr, cm^{-1}): 3074w, 3061w, 1480m, 1461s, 1434s, 1403s, 1305vs, 1238s, 1153vs, 1123s, 1094s, 1008s, 8067s, 753m, 739m, 694vs, 590m, 555m, 518s, 509s, 432s. ^1H NMR (DMSO-d^6, δ in ppm): δ 8.19–8.14 (m, 1H, H6); 8.06–8.00 (m, 1H, H3); 7.97–7.88 (m, 2H, H4/H5); 7.72–7.54 (m, 30 H, PPh_3). $^{31}P\{^1H\}$ NMR (DMSO-d^6, δ in ppm): δ 53.06 (PPh_3).

2.2.3. Tetrakis(thiosaccharinato)bis{bis(diphenylphosphino)methane} tetracopper(I) bis(dichloromethane), $[Cu_4(tsac)_4(dppm)_2] \cdot 2CH_2Cl_2$ (**4**)

A solution of **1** (0.012 g, 0.010 mmol) in acetonitrile (5 mL) was slowly added with constant mechanical stirring to a solution of bis(diphenylphosphino)methane (dppm) (0.0078 g, 0.020 mmol) in the same solvent (3 mL) (Cu/dppm molar ratio = 1/0.5). The resulting orange solution was evaporated to dryness at 40 °C. Dichloromethane (4 mL) was used to dissolve the solid and diethyl ether was allowed to slowly diffuse into the solution, at room temperature. The orange crystals obtained loosed their quality after exposure to moisture. The best crystals were kept in the mother liquor until they were mounted on a goniometric head for the X-ray diffraction study. To ensure the analytical composition of the substance, it was grinding and heated at 40 °C until constant weight was reached. *Anal.* Calc. for $C_{78}H_{60}Cu_4N_4O_8P_4S_8$: C, 51.6; H, 3.3; N, 3.1. Found: C, 51.9; H, 3.0; N, 2.6%. IR (freshly prepared solid, Nujol mulls, cm^{-1}): 1482w, 1436m, 1409m, 1338m, 1325m, 1244m, 1171s, 1154m, 1123m, 1020m, 1007m, 822m, 801m, 771m, 736m, 694m, 624w, 596m, 561m, 552m, 517w, 500vw, 428w. IR (solid, KBr, cm^{-1}): 3053w, 2923w, 1459s, 1437m, 1399m, 1323m, 1243s, 1169vs, 1123m, 1020m, 1004w, 818w, 739m, 694m, 595m, 560s, 437w. ^1H NMR (DMSO-d^6, δ in ppm): δ 8.03–7.92 (m, 2H, H6), 7.90–7.70 (m, 2H, H3), 7.70–7.48 (m, 4H, H4/H5); 7.15–6.70 (m, 8H, Ha), 7.45–7.15 (m, 12H, Hb, c), 3.48 (s, 2H, CH_2). $^{31}P\{^1H\}$ NMR (DMSO-d^6, δ in ppm): δ 48.95 (dppm).

2.2.4. Bis(thiosaccharinato)bis{bis(diphenylphosphino)methane} dicopper(I)dichloromethane, $[Cu_2(tsac)_2(dppm)_2] \cdot CH_2Cl_2$ (**5**)

Complex **5** was prepared at room temperature by the reaction of complex **1** (0.012 g, 0,010 mmol) and dppm (0.016 g, 0,040 mmol) in dried acetonitrile (2.5 mL) at room temperature (Cu/dppm molar ratio = 1/1). The resulting yellow solution was evaporated to dryness and the residual solid further dried in the oven at 40 °C. The yellow solid obtained was dissolved in dichloromethane (2 mL) and small amounts of well formed crystals were obtained by slow diffusion of dried diethyl ether. Yield: variable, around 10%. *Anal.* Calc. for $C_{65}H_{54}Cu_2Cl_2N_2O_4P_4S_4$: C, 56.7; H, 4.0; N, 2.0. Found: C, 57.3; H, 4.1; N, 2.3%. IR (KBr, cm^{-1}): 3054w, 2924w, 1482w, 1458s, 1434s, 1403s, 1364m, 1313s, 1300s, 1244m, 1166vs, 1151vs, 1121s, 1097m, 1022m, 1001s, 834w, 822m, 783m, 770m, 739vs, 693vs, 588m, 561m, 553m, 517m, 432s. Due to the low yield of the preparation, the NMR spectra were obtained dissolving corresponding amounts of complex **1** and dppm in DMSO-d^6, checking the resulting solutions by UV–Vis spectroscopy. ^1H NMR (DMSO-d^6, δ in ppm): δ 7.44–7.37 (m, 1H, H6), 7.19–7.11 (m, 1H, H3), 7.09–6.98 (m, 2H, H4/H5); 6.83–6.63 (m, 8H, Ha), 6.52-6.42 (m, 4H, Hc), 6.40–6.28 (m, 8H, Hb); 2.92 (s, 2H, CH_2). $^{31}P\{^1H\}$ NMR (DMSO-d^6, δ in ppm): δ 46.35 (dppm).

2.3. X-ray structure determination of complexes **2–5**

Crystal data, structure solution methods and refinement results are summarized in Table 1. The hydrogen atoms were stereochemically positioned and refined with the riding model, adopting an isotropic thermal parameter 20% greater than the equivalent isotropic displacement parameter of the corresponding C-atom to which they are bonded. This percentage was set to 50% for the methyl hydrogen atoms of the acetronitrile molecule in **2**, which were refined as a rigid group allowed to rotate around the corresponding C–CN bond.

Tables containing complete information on atomic coordinates and equivalent isotropic parameters, full intra-molecular bond distances and angles, anisotropic thermal parameters and hydrogen atomic positions are available from the authors upon request and

Table 1

Crystal data and structure solution methods and refinement results for $[Cu_4(tsac)_4(PPh_3)_3] \cdot MeCN$ (**2**), $[Cu(tsac)(PPh_3)_2]$ (**3**), $[Cu_4(tsac)_4(dppm)_2] \cdot 2CH_2Cl_2$ (**4**), and $[Cu_2(tsac)_2(dppm)_2] \cdot CH_2Cl_2$ (**5**).

	(**2**)	(**3**)	(**4**)	(**5**)
Empirical formula	$C_{84}H_{64}Cu_4N_5O_8P_3S_8$	$C_{43}H_{34}CuNO_2P_2S_2$	$C_{82}H_{68}Cl_8Cu_4N_4O_8P_4S_8$	$C_{65}H_{54}Cl_2Cu_2N_2O_4P_4S_4$
Formula weight	1875.08	786.37	1077.8	1377.31
Temperature (K)	296(2)	293(2)	293(2)	296(2)
Crystal system	triclinic	monoclinic	triclinic	triclinic
Space group	$P\bar{1}$	Pn	$P\bar{1}$	$P\bar{1}$
Unit cell dimension[a]				
a (Å)	13.1400(10)	11.1510(17)	12.6360(6)	13.1210(10)
b (Å)	16.5840(10)	12.6190(11)	13.5520(5)	13.335(2)
c (Å)	19.7850(10)	13.4310(18)	14.3610(6)	19.9020(10)
α (°)	91.650(10)	90.00	89.568(2)	93.910(10)
β (°)	94.120(10)	94.870(11)	71.953(2)	104.440(10)
γ (°)	107.380(10)	90.00	71.385(2)	107.310(10)
V (Å^3)	4098.2(4)	1883.1(4)	2204.49(16)	3181.1(6)
Z	2	2	2	2
D_{Calc} (Mg/m^3)	1.503	1.387	1.624	1.438
Absorption coefficient (mm^{-1})	1.344	2.957	1.513	4.166
$F(000)$	1890	812	1092	1412
Crystal size (mm)	0.21 × 0.11 × 0.04	0.32 × 0.2 × 0.06	0.19 × 0.14 × 0.12	0.32 × 0.24 × 0.24
Crystal color/shape	red/polyhedral	yellow/polyhedral	orange/polyhedral	yellow/polyhedral
Diffractometer/scan	KappaCCD/φ and ω	Enraf-Nonius CAD4/$\omega - 2\theta$ scan	KappaCCD/φ and ω	Enraf-Nonius CAD4/$\omega - 2\theta$ scan
Radiation, graphite monochramated (Å)	Mo Kα, $\lambda = 0.71073$	Cu Kα $\lambda = 1.54184$	Mo Kα, $\lambda = 0.71073$	Cu Kα $\lambda = 1.54184$
θ Range data collection (°)	2.80–25.0	3.50–72.05	2.69–25.00	2.32–67.99
Index ranges	$-15 \leqslant h \leqslant 15$, $-19 \leqslant k \leqslant 18$, $-23 \leqslant l \leqslant 23$	$-13 \leqslant h \leqslant 13$, $-1 \leqslant k \leqslant 15$, $0 \leqslant l \leqslant 16$	$-15 \leqslant h \leqslant 15$, $-16 \leqslant k \leqslant 16$, $-17 \leqslant l \leqslant 15$	$-15 \leqslant h \leqslant 15, 0 \leqslant k \leqslant 16, -23 \leqslant l \leqslant 23$
Reflections collected/unique	35 643/14 357	3890/3872	17 628/7715	12 112/11 572
R(int)	0.0595	0.0177	0.0560	0.0259
Observation reflections [$I > 2\sigma(I)$]	9705	3851	5614	9874
Completeness (%)	99.3	99.7	99.5	99.9
Maximum and minimum transmission	0.9444/0.8203	0.9603/0.8576	0.8672/0.7838	0.3783/0.4647
Data collection	COLLECT [23]	CAD4 express	COLLECT [23]	CAD4 express
Data reduction and correction[b]	DENZO and SCALEPACK [24]	XCAD4	DENZO and SCALEPACK [24]	XCAD4
Absorption correction	PLATON [25]			
Structure solution[c]	SHELXS-97 [26]			
Structure refinement[d]	SHELXL-97 [27]			
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Weights, $w(P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/3)$	$[\sigma^2(F_o^2) + (0.0374P)^2 + 5.66P]^{-1}$	$[\sigma^2(F_o^2) + (0.0586P)^2 + 0.31P]^{-1}$	$[\sigma^2(F_o^2) + (0.1180P)^2 + 6.2764P]^{-1}$	$[\sigma^2(F_o^2)+(0.0971P)^2 + 3.1349P]^{-1}$
Data/restraints/parameters	14 357/0/995	3872/2/461	7715/0/532	11 572/0/769
Goodness-of-fit on F^2	1.017	1.101	0.932	1.051
Final R-index [$I > 2\sigma(I)$][e]				
R_1/wR_2	0.0469/0.1122	0.0306/0.0802	0.0574/0.1548	0.0568/0.1510
R índices (all data)R_1/wR_2	0.0820/0.1311	0.0307/0.0803	0.0839/0.1797	0.0651/0.1619
Largest peak and hole (e A^{-3})	0.550/−0.589	0.449/−0.442	2.942/−2.356	0.756/−0.710

[a] Least-squares refinement of the angular settings for 35643 reflections in the $2.80 < \theta < 25.00°$ range for **2**, 25 reflections in the $32.23 < \theta < 67.32°$ range for **3**, 17 628 reflections in the $2.69 < \theta < 25.00°$ range for **4,** and 25 reflections in the $19.34 < \theta < 51.60°$ range for **5**.

[b] Corrections: Lorentz, polarization and absorption.

[c] Structure solved by direct and Fourier methods.

[d] Neutral scattering factors and anomalous dispersion corrections. Final molecular model obtained by anisotropic full-matrix least-squares refinement of the non-hydrogen atoms.

[e] R-indices defined as: $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

have been deposited at the Cambridge Crystallographic Data Centre, under deposition numbers CCDC 700159 (**2**), 700160 (**3**), 700161 (**4**), and 700162 (**5**).

3. Results and discussion

3.1. Structural results and discussion

3.1.1. Crystal and molecular structure of $[Cu_4(tsac)_4(PPh_3)_3] \cdot MeCN$ (2)

Selected bond lengths and angles in $[Cu_4(tsac)_4(PPh_3)_3] \cdot MeCN$ are listed in Table 2 and an ORTEP [28] molecular diagram of the complex is shown in Fig. 1.

The molecular complex is built over four Cu(I) cations held together by four thiosaccharinate anions, each one bridging three metals in a tripodal μ_3-N,S (η^2-S, η^1-N) coordination form. Three PPh_3 molecules bonded to three of the copper atoms of the tetramer completes the non-symmetric structure. Then all copper atoms are surrounded by two sulfur atoms and one nitrogen atom belonging to tsac anions and three of them are also bounded to one phosphorous atom of the phosphane molecules. The Cu···Cu distances are too long to be considered as bond distances and only for the Cu(1)–Cu(3) separation (2.9844(8) Å) a weak inter-metallic interaction can be considered. The tetra-nuclear unit of Cu(I) atoms resembles that of complex **1**. The inter-metallic distances are shorter in the last substance (between 2.6033(7) and

4.4909(9) Å) and the Cu–S bonds (between 2.2291(1) and 2.5319(1) Å) are longer than in complex **2** [15]. These structural changes are not the most important upon the coordination of the PPh_3 molecules. In the more asymmetric tetra-nuclear cluster of complex **1**, two Cu atoms are surrounded by two S atoms and one N atom of tsac anions and one N atom of a MeCN molecule, one of the metals is coordinated by three S atoms and with weak interactions to other two Cu atoms, and the forth Cu(I) center is surrounded by two N atoms of tsac anions and with a weak interaction to a S atom. These characteristics are indicating that a structural reorganization takes place in solution and complex **2** is not formed by coordination of the phosphane molecules over complex **1**. Both compounds **1** and **2** are bright red in the solid state and in solution, which can indicate that each complex retains its molecular arrangement in solution.

Table 2
Bond distances (Å) and angles (°) around copper in $[Cu_4(tsac)_4(PPh_3)_3] \cdot MeCN$ (**2**).

Bond distances			
Cu(1)–N(2)	2.055(3)	Cu(2)–Cu(3)	2.9207(7)
Cu(1)–P(5)	2.288(1)	Cu(3)–N(3)	2.001(3)
Cu(1)–S(41)	2.342(1)	Cu(3)–S(21)	2.186(1)
Cu(1)–S(11)	2.425(1)	Cu(3)–S(11)	2.228(1)
Cu(2)–N(4)	2.038(3)	Cu(4)–N(1)	2.062(3)
Cu(2)–P(7)	2.299(1)	Cu(4)–P(6)	2.301(1)
Cu(2)–S(31)	2.389(1)	Cu(4)–S(41)	2.341(1)
Cu(2)–S(21)	2.445(1)	Cu(4)–S(31)	2.349(1)
Bond angles			
N(2)–Cu(1)–P(5)	123.19(9)	S(31)–Cu(2)–Cu(3)	74.25(3)
N(2)–Cu(1)–S(41)	109.50(9)	S(21)–Cu(2)–Cu(3)	47.07(3)
P(5)–Cu(1)–S(41)	105.18(4)	N(3)–Cu(3)–S(21)	118.3(1)
N(2)–Cu(1)–S(11)	112.68(10)	N(3)–Cu(3)–S(11)	108.3(1)
P(5)–Cu(1)–S(11)	96.58(4)	S(21)–Cu(3)–S(11)	130.90(4)
S(41)–Cu(1)–S(11)	108.44(4)	N(3)–Cu(3)–Cu(2)	90.11(9)
N(2)–Cu(1)–Cu(3)	79.78(9)	S(21)–Cu(3)–Cu(2)	54.96(3)
P(5)–Cu(1)–Cu(3)	143.84(4)	S(11)–Cu(3)–Cu(2)	142.37(4)
S(41)–Cu(1)–Cu(3)	89.80(3)	N(3)–Cu(3)–Cu(1)	144.77(9)
S(11)–Cu(1)–Cu(3)	47.27(3)	S(21)–Cu(3)–Cu(1)	91.58(3)
N(4)–Cu(2)–P(7)	124.9(1)	S(11)–Cu(3)–Cu(1)	53.08(3)
N(4)–Cu(2)–S(31)	106.97(9)	Cu(2)–Cu(3)––Cu(1)	93.12(2)
P(7)–Cu(2)–S(31)	98.76(4)	N(1)–Cu(4)–P(6)	122.87(9)
N(4)–Cu(2)–S(21)	102.06(9)	N(1)–Cu(4)–S(41)	108.1(1)
P(7)–Cu(2)–S(21)	106.59(4)	P(6)–Cu(4)–S(41)	100.52(4)
S(31)–Cu(2)–S(21)	119.00(4)	N(1)–Cu(4)–S(31)	110.3(1)
N(4)–Cu(2)–Cu(3)	103.54(9)	P(6)–Cu(4)–S(31)	102.12(4)
P(7)–Cu(2)–Cu(3)	130.42(4)	S(41)–Cu(4)–S(31)	112.65(4)

The molecular structure of solid complex **2** is very similar to that observed for $Ag_4(tsac)_4(PPh_3)_3$ complex [22b]. In this substance all the tsac anions are also coordinated to three metal centers in μ_3-S,N coordination mode and only three silver atoms are coordinated by PPh_3 molecules. As a difference with the copper complex, obtained by the reaction with PPh_3, the silver thiosaccharinate needs the presence of a weak nitrogenous base to be obtained. There is only one closed tetra-nuclear copper–thionate–PPh_3 complex reported in the literature, namely the $Cu_4(tzdt)_4(PPh_3)_2$ (tzdt = thiazolidine-2-thione) complex. Like other binary copper thionates it crystallizes as *butterfly-shaped*

Table 3
Bond distances (Å) and angles (°) around copper in $[Cu(tsac)(PPh_3)_2]$ (**3**).

Bond distances			
Cu–P(2)	2.2504(8)	S(1)–C(1)	1.689(3)
Cu–P(1)	2.2658(8)	N–C(1)	1.320(4)
Cu–S(1)	2.2753(9)		
Bond angles			
P(2)–Cu–P(1)	122.38(3)	C(1)–S(1)–Cu	98.1(1)
P(2)–Cu–S(1)	124.78(3)	N–C(1)–S(1)	124.6(2)
P(1)–Cu–S(1)	112.73(3)		

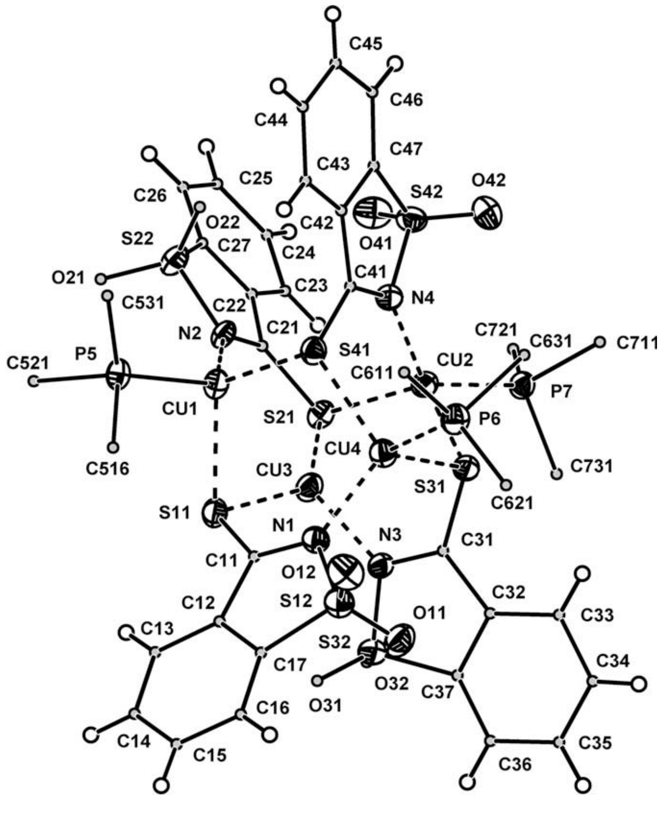


Fig. 1. Molecular plot of $Cu_4(tsac)_4(PPh_3)_3$ (**2**) showing the labeling scheme of the non-H atoms. For clarity, the carbon atoms are indicated by small gray disks and only the bonded-to-phosphorous C-atom of the phenyl groups are included in the plot. Displacement ellipsoids of the other non-H atoms are drawn at the 30% probability level. Copper-ligand bonds are indicated by dashed lines.

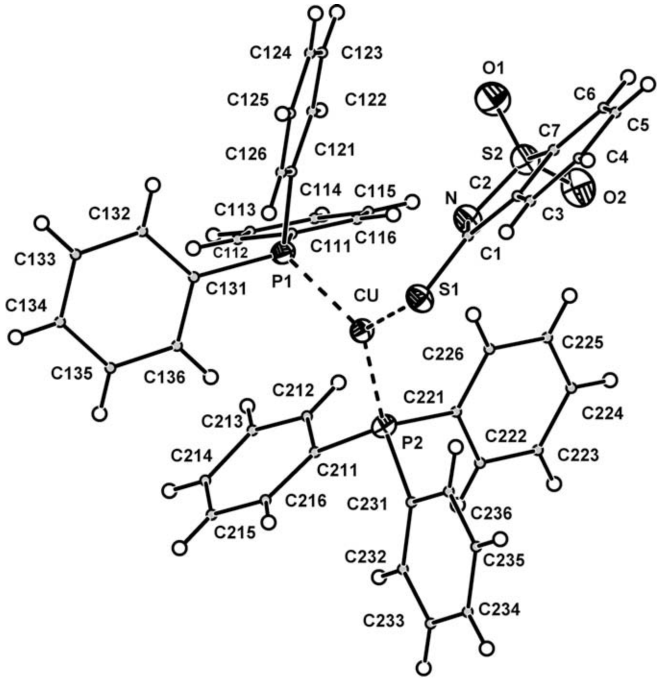


Fig. 2. Molecular plot of $Cu(tsac)(PPh_3)_2$ (**3**) showing the labeling scheme of the non-H atoms. For clarity, the carbon atoms are indicated by small gray disks and only the bonded-to-phosphorous C-atom of the phenyl groups are included in the plot. Displacement ellipsoids of the other non-H atoms are drawn at the 30% probability level. Copper-ligand bonds are indicated by dashed lines.

units with smaller copper–copper distances (between 2.741 and 2.992 Å) and very similar Cu–S bond lengths (between 2.191 and 2.424 Å) [14d].

3.1.2. Crystal and molecular structure of [Cu(tsac)(PPh_3)$_2$] (**3**)

Complex **3** crystallizes as a mononuclear molecular compound. A selection of bond distances and angles of **3** are listed in Table 3 and its molecular plot is presented in Fig. 2.

The Cu(I) ion is in a slightly distorted trigonal planar coordination sphere, bonded by the exocyclic sulfur atom of a thiosaccharinate anion and by two phosphorous atoms of two triphenylphosphane molecules. The Cu–S bond length is shorter than the average values obtained for complexes **1** and **2** (2.341(1) and 2.338(1) Å, respectively), in accordance with the change of coordination mode from tri-coordinated bridge to mono-coordinated. As far as we know the molecular structure of complex **3** is quite unique. There are many examples of poly-nuclear copper thionates reported in the literature [14–21], but only one report of a mononuclear copper-thionate-triphenylphosphane structure, the [Cu(pymt)(PPh_3)$_2$] (pymt: pyrimidine-2-thionato) complex of Ruan and Shi [17a]. The pymt ions act as κ^2-S,N chelating ligands (Cu–S and Cu–N distances of 2.4023(7) and 2.139(2) Å, respectively) and the exocyclic sulfur atoms have distal interactions with other copper atoms of neighbor complexes, making a two-dimensional network. More common are the tetracoordinated CuX(PPh_3)$_2$HL complexes (X: halide, HL: neutral thione) [13]. As can be expected, the Cu–S distance in complex **3** is shorter than those reported for neutral thione complexes, as CuI(PPh_3)$_2$(bzimtH_2) (2.3692(8) Å) and CuI(PPh_3)$_2$(bztztH) (2.3660(6) Å) (bzimtH_2: benzimidazole-2-thione, and bztztH: benzothiazole-2-thione) [13g], CuCl(PPh_3)$_2$ (pytH) (2.381(2) Å) (pytH: pyridine-2-thione) [13h], or CuCl (PPh_3)$_2$(pymtH) (2.3875(7) Å) (pymtH: pyrimidine-2-thione) [13f]. The Cu–P bond lengths are very similar to those reported for [Cu(pym2S)(PPh_3)$_2$] (2.2417(7) and 2.2557(7) Å) [17a] and shorter than the distances observed in related copper-thione complexes, such as CuCl(PPh_3)$_2$(pytH) (2.300(2) and 2.288(2) Å) [13h], or CuCl(PPh_3)$_2$(pymtH) (2.2899(6) and 2.2978(6) Å) [13f].

The triphenylphosphane ligands show internal bond lengths and angles typical for this molecule coordinated to Cu(I) metal centers [13f–h,17a]. For the thionate anion the C–S bond distance is longer and the C–N bond shorter than the corresponding parameters of free thiosaccharin (1.624(2) and 1.384(3) Å, respectively [29]), showing the expected electronic charge delocalization upon deprotonation and coordination [30]. These parameters are very close to that observed for metal thiosaccharinates in which the thionates are mono-coordinated through the exocyclic S atom (C–S and C–N) distances of 1.7022/1.6965 and 1.312/1.314 Å, respectively for Cd(tsac)$_2$(bim)$_2$ [22e] and 1.673(5) and 1.334(6) Å, respectively, for Ag(tsac)(PPh_3)$_2$ [22b].

3.1.3. Crystal and molecular structure of [Cu_4(tsac)$_4$(dppm)$_2$] · $2CH_2Cl_2$ (**4**)

Complex **4** has a very curious structure consisting on centrosymmetric tetranuclear molecules. Selected bond lengths and angles are listed in Table 4 and a molecular diagram of the compound is presented in Fig. 3.

The two halves of each molecule are copper dimers, 'Cu_2(tsac)$_2$(dppm)', bridged through the exocyclic S atoms of thiosaccharinate anions, in a Cu_2S_2 dinuclear planar arrangement (S(21)–Cu(2)–S(21)^i = 86.01(5) and Cu(2)–S(21)–Cu(2)^i = 93.99(5)°). Thus, only half of the molecule will be discussed. The Cu2···Cu2^i distance is 3.566(1) Å, too long for significant metal–metal interaction. In the 'Cu_2(tsac)$_2$(dppm)' subunits the Cu(2)–Cu(1) distance (2.8494(9) Å) is in the order of the sum of the van der Waals radii of copper atoms (2.80 Å) [31] and therefore suggesting the existence of interaction between the Cu(I) centers, as was already pointed out by Cotton and col. for 'Cu_2(dppm)$_2$' di-bridged frameworks [19b]. Cu(2) binds to three exocyclic S-atoms from three thiosaccharinates, to one P atom belonging to one dppm molecule and to the Cu(1) atom in a fivefold coordination. Cu(1) is surrounded by two N atoms from two thionates, one P atom of the dppm molecule and the Cu(2) atom, in a trigonal pyramidal geometry. The major deviations from the ideal values (120° and 90°) are the angles in the trigonal plane, which range from 105.4(2)° to 137.5(1)°. It should be observed that the asymmetric coordination of the tsac ligands in each 'Cu_2(tsac)$_2$(dppm)' subunit (two S atoms over Cu(2) and two N atoms over Cu(1)), named *head-to-head* [1b], is unknown in the chemistry of copper(I) thionates. Such type of dinuclear arrangements have been observed for [Ag_2(tsac)$_2$(py)] [22a], and more examples exist of dinuclear metal thionates with the symmetric *head-to-tail* arrangement [32]. These type of coordination form of the tsac anions might have synergic effects with the existence of the S-atom bridges between the 'Cu_2(tsac)$_2$(dppm)' subunits.

Table 4
Bond distances (Å) and angles (°) around copper in [Cu_4(tsac)$_4$(dppm)$_2$] · $2CH_2Cl_2$ (**4**).

Bond distances			
P(2)–Cu(2)	2.241(2)	Cu(2)–Cu(1)	2.8494(9)
S(11)–Cu(2)	2.272(2)	P(1)–Cu(1)	2.205(1)
S(21)–Cu(2)	2.371(2)	N(1)–Cu(1)	1.985(4)
S(21)^i–Cu(2)	2.503(1)	N(2)–Cu(1)	2.057(5)
Bond angles			
P(2)–Cu(2)–S(11)	130.49(6)	S(21)–Cu(2)–Cu(1)	79.29(4)
P(2)–Cu(2)–S(21)	104.31(6)	S(21)^i –Cu(2)–Cu(1)	154.17(4)
P(2)–Cu(2)–S(21)^i	118.37(5)	P(1)–Cu(1)–N(1)	137.5(1)
P(2)–Cu(2)–Cu(1)	86.03(4)	P(1)–Cu(1)–N(2)	116.7(1)
S(11)–Cu(2)–S(21)	119.52(6)	P(1)–Cu(1)–Cu(2)	95.44(4)
S(11)–Cu(2)–S(21)^i	88.12(5)	N(1)–Cu(1)–N(2)	105.4(2)
S(11)–Cu(2)–Cu(1)	80.96(4)	N(1)–Cu(1)–Cu(2)	92.6(1)
S(21)–Cu(2)–S(21)^i	86.01(5)	N(2)–Cu(1)–Cu(2)	87.0(1)

Symmetry codes: (i) $-x + 1, -y + 1, -z + 2$.

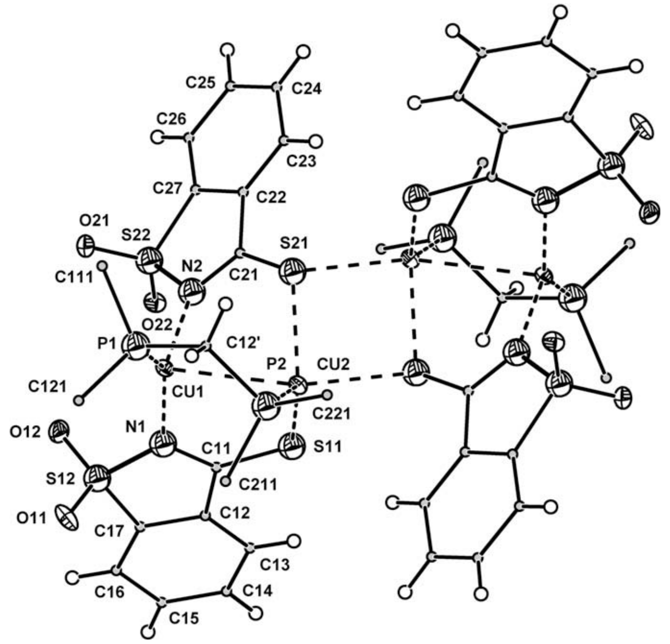


Fig. 3. Molecular plot of Cu_4(tsac)$_4$(dppm)$_2$ (**4**) showing the labeling scheme of the non-H atoms. For clarity, the carbon atoms are indicated by small gray disks and only the bonded-to-phosphorous C-atom of the phenyl groups are included in the plot. Displacement ellipsoids of the other non-H atoms are drawn at the 30% probability level. Copper-ligand bonds are indicated by dashed lines.

As far as we know there are only two reports of triply-bridged dinuclear Cu(I) complexes with one bridging dppm molecule. One of them is a copper thionate, $[Cu_2({}^tBuMe_2Si\text{-}py2S)_2(dppm)_2]$ (${}^tBuMe_2Si$-py2S = 6-tert-butyldimethylsilyl-pyridine-2-thionate) [17b], in which the two thionate anions made the remaining two bridges of the structure. The Cu···Cu distance (2.711(2) Å) is one of the shortest distances reported for a dinuclear 'Cu_2(dppm)' framework. It has a very asymmetric structure, with the second dppm molecule mono-coordinated to only one of the Cu ions by a P-atom and with the two thionates bridging the Cu(I) centers in different coordination forms, one in a μ_2-S, and the other in a μ_2-N,S arrangement [17b]. The second related complex is a copper dithiocarboxilate with a very similar structure to complex **4**. It also consists of tetra-nuclear molecular units $[Cu_2(S_2CT)_2(dppm)]_2$ (S_2CT = dithio-o-toluato-κ^2-S,S′) build by two dinuclear halves. Each '$Cu_2(S_2CT)_2$(dppm)' subunit has a dppm and two S_2CT bridges, with a bit longer Cu···Cu distance of 2.874(4) Å. One of the S atoms of one of the dithio-*o*-toluate anions is also coordinated to the corresponding Cu atoms of the other subunit, defining a centrosymmetric tetranuclear molecule [17b]. The Cu–S bond lengths of the bridges (2.341(4) and 2.565(5) Å) are in the order of the observed distances for complex **4**.

Table 5
Bond distances (Å) and angles (°) around copper in $[Cu_2(tsac)_2(dppm)_2] \cdot CH_2Cl_2$ (**5**).

Bond distances			
Cu(2)–N(1)	1.988(3)	Cu(1)–P(1)	2.2961(9)
Cu(2)–P(2)	2.2333(9)	Cu(1)–S(11)	2.3065(10)
Cu(2)–P(4)	2.2695(9)	Cu(1)–P(3)	2.3212(9)
		Cu(1)–S(21)	2.4095(11)
Bond angles			
N(1)–Cu(2)–P(2)	128.39(9)	S(11)–Cu(1)–P(3)	119.50(4)
N(1)–Cu(2)–P(4)	115.41(9)	P(1)–Cu(1)–S(21)	96.76(4)
P(2)–Cu(2)–P(4)	115.28(4)	S(11)–Cu(1)–S(21)	97.20(4)
N(1)–Cu(2)–Cu(1)	90.76(8)	P(3)–Cu(1)–S(21)	106.40(4)
P(2)–Cu(2)–Cu(1)	96.54(3)	P(1)–Cu(1)–Cu(2)	79.42(3)
P(4)–Cu(2)–Cu(1)	92.05(3)	S(11)–Cu(1)–Cu(2)	77.51(3)
P(1)–Cu(1)–S(11)	121.32(4)	P(3)–Cu(1)–Cu(2)	83.36(3)
P(1)–Cu(1)–P(3)	110.25(4)	S(21)–Cu(1)–Cu(2)	170.24(4)

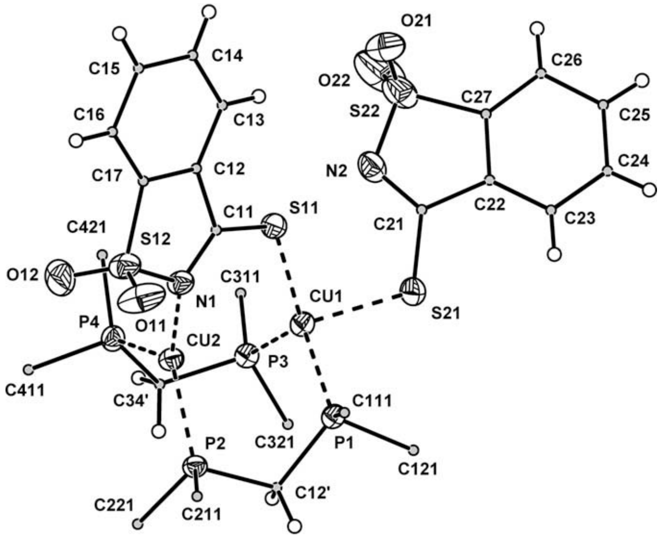


Fig. 4. Molecular plot of $Cu_2(tsac)_2(dppm)_2$ (**5**) showing the labeling scheme of the non-H atoms. For clarity, the carbon atoms are indicated by small gray disks and only the bonded-to-phosphorous C-atom of the phenyl groups are included in the plot. Displacement ellipsoids of the other non-H atoms are drawn at the 30% probability level. Copper-ligand bonds are indicated by dashed lines.

3.1.4. Crystal and molecular structure of complex $[Cu_2(tsac)_2(dppm)_2] \cdot CH_2Cl_2$ (5)

Selected bond distances and angles for the dinuclear complex **5** are listed in Table 5 and a molecular diagram of the molecule is shown in Fig. 4.

$[Cu_2(tsac)_2(dppm)_2]$ complex shows also a uncommon asymmetric triply bridged di-copper(I) core, with different environments around each metal center due to the different coordination forms of the anions, one as a μ_2-N,S coordinating and the other as a S-monocoordinating ligand. Cu(1) atom binds to two P-atoms of different dppm molecules, and the two exocyclic S atoms of the thiosaccharinates, one belonging to the bridging thionate and the other to the mono-coordinated one, in a highly distorted tetrahedral environment. Cu(2) binds to one N atom of the bridging thiosaccharinate ligand and to the other two P-atoms of the diphosphanes, in a distorted trigonal planar arrangement. The Cu(2)···Cu(1) distance (3.0351(9) Å) is greater than the sum of the van der Waals radii of copper atoms (2.80 Å) [31] and therefore too long to qualify as a metal–metal bond. The Cu···Cu distance in **5** falls between the 3.757(3) Å value observed for $[Cu_2(dppm)_2(MeCN)_4](ClO_4)_2$, a complex without coordinated anions [19f], and the 2.7883(11), 2.707(1), and 2.679(6) Å values reported for $[Cu_2(dppm)_2(MeCOO)](BF_4)$ [19c], $[\{Cu_2(dppm)_2\}_2(OOCC_6H_4COO)](PF_6)_2$ [19b], and $[Cu_2(dppm)_2(MeC_5H_3NO)](ClO_4)$ (MeC_5H_3NO = 6-methyl-pyridin-2-olate) [19e], respectively. In the last complexes the organic anions strongly coordinate the Cu(I) nuclei of the '$Cu_2(dppm)_2$' frameworks acting as third bridging ligands, and for them weak Cu···Cu interaction are to be expected [19b]. The Cu···Cu separation in complex **5** is very similar to the 3.1003(9) Å distance observed for $[Cu_2(dppm)_2(CN^tBu)_3](BF_4)_2$ where one of the isonitrile ligands binds the copper centers in a μ_2-C arrangement [19a].

The presence of the bridging dppm ligands in complexes of this kind imparts unusual stability to the '$Cu_2(dppm)_2$' framework [19b]. The Cu–P bond lengths are quite similar to those reported for other copper diphosphane complexes, like $[Cu_2(dppm)_2(MeCN)_4](ClO_4)_2$ (2.270(3) and 2.283(3) Å) [19f], but longer than the bond lengths reported for $[Cu_2(dppm)_2(MeCOO)](BF_4)$ (from 2.258(2) to 2.241(2) Å), a complex with a shorter Cu···Cu distance [19c].

As mentioned above, there are two different coordination modes for the thiosaccharinate ligands. One of them bridges the Cu atoms in a μ_2-N,S coordination form. The other one binds only one of the Cu atoms as a mono-coordinated η^1-S ligand. The different coordination modes are reflected in the internal bond distances of the tsac anions. The bridging one has a shorter exocyclic C–S bond distance (1.664(4) Å) than the mono-coordinated anion (1.686(4) Å), indicating a greater negative charge delocalization over the thiocarbonilic functional group in the later ligand.

3.2. Vibrational and electronic spectra of solid complexes

The solid state FT-IR spectra of the complexes **1**–**5**, recorded between 4000 and 400 cm^{-1} in KBr pellets or in Nujol mulls, provide information regarding the coordination mode of the thiosaccharinate ligand and confirm the presence of the phosphanes. Table 6 shows the IR assignments for the most important bands related to vibrations of the five-membered ring of the thionate anion in the complexes. Those assignments are based on general information of thiosaccharin and thiosaccharinate anion analyzed and discussed in previous papers [22b,33]. The disappearance of the ν(NH) band of the free thiosaccharin is verified in combination with the lack of any ν(SH) bands at 2600–2500 cm^{-1}, indicating that the thione ligand is in the deprotonated form in these complexes. Among the observed bands (Table 6), those principally belonging to the stretching motion of the thiocarbonyl and imino bonds of the thiosaccharinate anion, ν(CS) and ν(CN), bring information about the coordination mode of the thionate. For the simplest structure of complex **3** with a two electron coordination of the tsac ligand through the exocyclic S atom, two sharp bands (1008 and 1403 cm^{-1}, respectively) have been observed. As a comparison, the bands of the 'free' tsac anion in the (PNP)tsac (PNP: bis(triphenylphosphino)iminium cation) lie at 1010, ν(CS), and 1365, ν(CN), cm^{-1}. In the tetranuclear complex **2**, all the tsac anions have a tripodal μ_3-N,S^2 coordination with longer C–S bonds (average value of 1.704 Å). It correlates with a ν(CS) band located at lower wavenumbers (Table 6).

As can be expected, more complex vibrational patterns are observed for complexes **4** and **5**. For the former, freshly prepared samples were dispersed in Nujol to obtain its IR spectra. As was discussed previously, two coordination forms of the tsac anions are present in complex **4**. The μ_2-N,S (one under a Nujol band, 1020, and 822 cm^{-1} bands) and the μ_3-N,S^2 (1409, 1007, and 801 cm^{-1} bands) bridging forms can be characterized. The IR spectra of complex **5** are in accord with the observed molecular structure too. The μ_2-N,S bridging thiosaccharinate display bands at different wavenumbers (1364, 1022, and 834 cm^{-1}) than the η^1-S coordinated anion (1403, 1001, and 822 cm^{-1}).

For all the complexes reported here, strong bands due to the coordinated triphenylphosphane or dppm ligands are observed in the medium IR region, in some cases masking less intense thiosaccharinate bands [34].

The solid state electronic absorption spectra of the complexes consist in three very broad bands appearing in the 220–250, 270–290, and 340–360 nm regions. The first two intense bands are unresolved mixtures that belong to $\pi \to \pi^*$ transitions of the phenyl rings of the phosphane ligands and of the benzene rings of the thiosaccharinate anions [35]. The weak lower energy bands lie in the region where free thiones absorb, and can be assigned to $\pi \to \pi^*$ and $n \to \pi^*$ transitions of the thiocarbonilic ($C=S$) bonds [36] but they are little sensitive to the coordination forms of the tsac ligands.

3.3. NMR spectra of complexes and reactivity of copper thiosaccharinate with phosphanes

As was previously mentioned, the red solid complex **1** brings also red solutions in MeCN or DMSO solvents. Its ^{1}H and ^{13}C NMR spectra in DMSO-d^6 show only one set of signals (for tsac, ^{1}H NMR: δ 8.17–7.99 (m, 1H, H6); 7.95–7.83 (m, 1H, H3); 7.83–7.69 ppm (m, 2H, H4/H5); ^{13}C NMR: tsac: δ 183.3 (C1); 134.9 (C7); 133.1(C4); 132.6(C5); 131.6 (C2); 124.8(C6); 119.8(C3)) [15] (see numbering code in Scheme 2). Complex **1** is a poly-nuclear species also in solutions of low coordinating solvents. In the presence of increasing amounts of PPh_3 or dppm, the original red solutions of complex **1** change to red–orange, at medium concentrations, and finally to bright yellow when a excess of phosphanes exists. At stoichiometric or quasi-stoichiometric molar ratios Cu:PPh_3 (or dppm) crystalline solids with the composition of the solutions can be isolated (see Scheme 2). With the aim to reproduce with Cu(I) thiosaccharinate the same structure reported for Ag(I), the $[Ag(tsac)(PPh_3)_3]$ compound [22b], synthetic routes with higher amounts of PPh_3 were used. Complex **3** was always recovered.

Table 6
FT-IR spectra and assignments for a selection of thiosaccharinate absorption bands in solid complexes $[Cu_4(tsac)_4(PPh_3)_3] \cdot MeCN$ (**2**), $[Cu(tsac)(PPh_3)_2]$ (**3**), $[Cu_4(tsac)_4(dppm)_2] \cdot 2CH_2Cl_2$ (**4**), and $[Cu_2(tsac)_2(dppm)_2] \cdot CH_2Cl_2$ (**5**).

Assignments	**1**[a]	**2**	**3**	4		**5**
				Nujol	KBr	
ν(CN), ν(ϕS)[b]	1417m[c]			1409m		1403s
	1405m	1399s	1403s	N[d]	1399m	1364m
$\nu_{as}(SO_2)$	1338s	1325s	1305vs	1338m	1323m	1313s
				1325m		1300s
ν_{as}(ϕCN), δ(CH)	1237s	1236s	1238s	1244m	1243s	1244m
$\nu_s(SO_2)$, ν(CC)	1176vs	1170vs	1153vs	1171s	1169vs	1166vs
				1154m		1151vs
$\nu_s(SO_2)$, δ(ϕSN)	1126m	1124s	1123s	1123m	1123	1121s
ν(CS), δ(CNS)				1020m	1020m	1022m
	1006m	1003s	1008s	1007m	1004w	1001s
	998w					
ν(NS), δ(CCC)	809w			822m	818w	834w
	800m	792m	806s	801m		822m

[a] Nujol mulls [15].
[b] ν: stretching; δ: in-plane deformation; γ: out-of-plane deformation; as: asymmetric; s: symmetric; ϕ: bencenic ring.
[c] vs: very strong; s: strong; m: medium; w: weak; vw: very weak.
[d] Strong Nujol band.

The four complexes, **2**–**5**, also show single sets of signals in their ^{1}H, and ^{31}P{1H} NMR spectra in DMSO-d^6 solutions, hence indicate the existence of only one species. The molar conductances of complexes **2** and **3**, similar to that reported for complex **1** (27 Ω^{-1} mol^{-1} cm^{-1}) [15] are in accord with that picture. For complexes **2** and **3** the signal of the PPh_3 molecules appears low-field shifted against the free ligand and at the same position (ca. 53 ppm) in the ^{31}P NMR of both complexes. The low-field shifting indicates that the PPh_3 molecules are still coordinated to the Cu atoms in solution. The solvation of the more accessible Cu center in complex **3** could be responsible of the similarity in the NMR responses between both complexes. They have small differences in Cu–P bond orders in the solid state (Tables 2 and 3), and the Cu–PPh_3 bonds could be weakened by the solvent in complex **3**. The ^{1}H NMR signals of the tsac anion in complex **3** appears low-field shifted against complex **2**, indicating that in solution a different coordination mode of the ligands also exists. The ^{1}H-NMR signals of **3** have chemical shifts similar to the neutral thiosaccharin. For Htsac: ^{1}H NMR: δ 8.17 (H6); 8.04 (H3); 8.02 (H5), 7.81 (H4) and 6.02 ppm (H1), which is in its thiol tautomeric form in DMSO-d^6 solutions [33]. This is in accordance with an anion monocoordinated to the Cu atom through the thiocarbonilic S atom. The ^{1}H NMR chemical shifts of complex **2** indicate a great delocalization of the negative electronic charge on the thioamidate functional groups. Therefore, the substance might be also a tetranuclear species in solution. As was already pointed out with the crystal discussions, the molecular structures of the '$Cu_4(tsac)_4$' tetramers in complexes **1** and **2** are different. A structural reorganization of complex **1** takes place in solution prior to or as a consequence of the Cu–P bonds formation.

The ^{31}P NMR signals of the dppm molecules of complexes **4** and of the mixtures with complex **5** stoichiometry appear low-field shifted against the free ligand (48.95 and 46.35 ppm, respectively). The low-field shifting confirms that in solution the two P atoms of the dppm molecules are both coordinated to the Cu atoms and that the dimeric 'Cu_2(dppm)' and '$Cu_2(dppm)_2$' frameworks exist also in the DMSO-d^6 solutions. The pattern and the chemical shifts of the ^{1}H NMR signals of the tsac anions of complex **4** indicate that its molecular structure doesn't change in solution. The ^{1}H NMR signals of complex **5** appear low field shifted compared to complex **4**. They resemble those of the free thiosaccharinate (for DMSO-d^6 solutions of NBu^t_4(tsac): ^{1}H NMR: δ 7.71 (H6); 7.45 (H3); and 7.40 (H4/H5) ppm) [33]. This would agree with the presence of two equivalent not coordinated anions in solution.

4. Conclusions

A wide range of mono and polymeric Cu(I)–thosaccharinate–phosphane complexes have been prepared and characterized, showing different coordination modes for the thionate ligands and different nuclearities. When enough triphenylphosphane is present, the simple mononuclear $Cu(tsac)(PPh_3)_2$ complex is formed. When the amount of the P-donor ligand is not enough to fill the coordination sphere of the metal atoms, then the poly-nuclear complex $Cu_4(tsac)_4(PPh_3)_3$ is obtained.

When a rigid diphosphane like dppm is used as a second ligand, poly-nuclear copper arrangements are always produced. As in the case of triphenylphosphane, when there is a lack of dppm the Cu nuclearity is high and a new and interesting tetra-nuclear Cu(I) complex is isolated.

5. Supplementary material

CCDC 700159, 700160, 700161 and 700162 contains the supplementary crystallographic data for **2**, **3**, **4** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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References

[1] (a) E.S. Rapper, Coord. Chem. Rev. 153 (1996) 199;
(b) E.S. Rapper, Coord. Chem. Rev. 165 (1997) 475;
(c) J.A. García-Vázquez, J. Romero, A. Sousa, Coord. Chem. Rev. 193–195 (1999) 691;
(d) P.D. Akrivos, Coord. Chem. Rev. 181–210 (2001) 213.
[2] A. Castiñeiras, I. García-Santos, S. Dehnen, P. Sevillano, Polyhedron 25 (2006) 3653.
[3] E. López-Torres, M. Mendiola, C.J. Pastor, Inorg. Chem. 45 (2006) 3103.
[4] P. Aslanidis, S. Divanidis, P.J. Cox, P. Karagiannidis, Polyhedron 24 (2005) 853.
[5] T.S. Lobana, R. Sharma, R. Sharma, S. Mehra, A. Castiñeiras, P. Turner, Inorg. Chem. 44 (2005) 6.
[6] J.A. García-Vazquez, A. Souza-Pedrares, M. Carabel, J. Romero, A. Souza, Polyhedron 24 (2005) 2043.
[7] L.M. Nguyen, M.E. Dellinger, J.T. Lee, R.A. Quinlan, A.L. Rheingold, R.D. Pike, Inorg. Chim. Acta 358 (2005) 1331.
[8] B. Krebs, G. Henkel, Angew. Chem., Int. Ed. Engl. 30 (1991) 769.
[9] (a) S. Stoyanov, T. Stoyanova, I. Antonov, P. Karagiannidis, P.D. Akrivos, Monatsch. Chem. 127 (1996) 495;
(b) S. Stoyanov, T. Stoyanova, P.D. Akrivos, Trends Appl. Spectrosc. 2 (1998) 89.
[10] E.S. Rapper, Coord. Chem. Rev. 129 (1994) 91.
[11] L.-O. Klotz, U. Weser, in: K.D. Rainsford, R. Milanino, J.R.J. Sorenson, G.P. Velo (Eds.), Copper and Zinc in Inflammatory and Degenerative Diseases, Kluwer Academic Publication, Dordrecht, 1998, p. 19.
[12] I.G. Dance, Polyhedron 5 (1986) 1037.
[13] (a) T.S. Lobana, R. Sultana, G. Hundal, Polyhedron 27 (2008) 1008;
(b) M. Mamais, P.J. Cox, P. Aslanidis, Polyhedron 27 (2008) 175;
(c) P.J. Cox, A. Kaltzoglou, P. Aslanidis, Inorg. Chim. Acta 359 (2006) 3183;
(d) K. Marjani, S.C. Davies, M.C. Durrant, D.L. Hughes, N. Khodamorad, Acta Cryst. Sect. E 62 (2006) 774;
(e) A. Kaltzoglou, P.J. Cox, P. Aslanidis, Inorg. Chim. Acta 358 (2005) 3048;
(f) D. Li, W.-J. Shi, T. Wu, S.W. Ng, Acta Cryst. Sect. E 60 (2004) 776;
(g) P. Aslanidis, P.J. Cox, P. Karagiannidis, S.K. Hadjikakou, C.D. Antoniadis, Eur. J. Inorg. Chem. (2002) 2216;
(h) T. Lobana, A. Castiñeiras, Polyhedron 21 (2002) 1603;
(i) P.J. Cox, P. Aslanidis, P. Karagiannidis, Polyhedron 19 (2000) 1615;
(j) P.J. Cox, P. Aslanidis, P. Karagiannidis, S.K. Hadjikakou, Polyhedron 18 (1999) 1501;
(k) P. Aslanidis, S.K. Hadjikakou, P. Karagiannidis, P.J. Cox, Inorg. Chim. Acta 271 (1998) 243;
(l) T. Shibahara, S. Kobayashi, D. Long, X. Xin, Acta Cryst. Sect. C53 (1997) 58.
[14] (a) M. Shi, J.-K. Jiang, Chirality 15 (2003) 605;
(b) E.S. Raper, J.R. Creighton, W. Clegg, L. Cucurull-Sanchez, M.N. Stuart Hill, P.D. Akrivos, Inorg. Chim. Acta 271 (1998) 57;
(c) J.A. García-Vázquez, J. Romero, R. Castro, A. Souza, D.J. Rose, J. Zubieta, Inorg. Chim. Acta 260 (1997) 221;
(d) C.A. Lopez, J.P. Fackler, R.J. Staples, S. Wang, R. Winpenny, Croat. Chem. Acta 68 (1995) 793;
(e) E.S. Raper, J.R. Creighton, W. Clegg, Inorg. Chim. Acta 237 (1995) 87;;
(f) J.P. Fackler Jr., C.A. Lopez, R.J. Staples, S. Wang, R.E.P. Winnipenny, R.P. Lattimer, J. Chem. Soc., Chem. Commun. (1992) 146;
(g) E.S. Raper, J.R. Creighton, W. Clegg, Inorg. Chim. Acta 183 (1991) 179.
[15] M. Dennehy, G.P. Tellería, S.H. Tarulli, O.V. Quinzani, S.D. Mandolesi, J.A. Güida, G.A. Echeverría, O.E. Piro, E.E. Castellano, Inorg. Chim. Acta 360 (2007) 3169.
[16] (a) J.A. García-Vázquez, J. Romero, A. Souza-Pedrares, M.L. Louro, A. Souza, J. Zubieta, J. Chem. Soc., Dalton Trans. (2000) 559;
(b) E.C. Constable, S.M. Elder, C.A. Palmer, P.R. Raithby, D.A. Tocher, Inorg. Chim. Acta 252 (1996) 281;
(c) R. Castro, M.L. Durán, J.A. García-Vázquez, J. Romero, A. Souza, E.E. Castellano, J. Zukerman-Schpector, J. Chem. Soc., Dalton Trans. (1992) 2559;
(d) S. Kitagawa, M. Munakata, H. Shimono, S. Matsuyama, H. Masuda, J. Chem. Soc., Dalton Trans. (1990) 2105;
(e) E. Block, M. Gernon, H. Kang, J. Zubieta, Angew. Chem., Int. Ed. Engl. 27 (1988) 1342.
[17] (a) C.-X. Ruan, W.-J. Shi, Acta Crystallogr. E63 (2007) m2412;
(b) P. Perez-Lourido, J. García–Vazquez, J. Romero, M.S. Louro, A. Souza, J. Zubieta, Inorg. Chim. Acta 271 (1998) 1;
(c) R. Castro, J. Romero, J.A. García-Vázquez, A. Souza, Y.D. Chang, J. Zubieta, Inorg. Chim. Acta 345 (1996) 119;
(d) E.W. Ainscough, E.N. Baker, A.G. Bingham, A.M. Brodie, C.A. Smith, J. Chem. Soc., Dalton Trans. (1989) 2167.
[18] C. di Nicola, C. Pettinari, M. Ricciutelli, B. Skelton, N. Somers, A.H. White, Inorg. Chim. Acta 358 (2005) 4003.
[19] (a) E. Fournier, F. Lebrun, M. Drouin, A. Decken, P.D. Harvey, Inorg. Chem. 43 (2004) 3127;
(b) P. Angaridis, F.A. Cotton, M.A. Petrukhina, Inorg. Chim. Acta 324 (2001) 318;
(c) P.D. Harvey, M. Drouin, T. Zhang, Inorg. Chem. 36 (1997) 4998;
(d) D. Li, C.-M. Che, W.-T. Wong, S.-J. Shieh, S.-M. Peng, J. Chem. Soc., Dalton Trans. (1993) 653;
(e) J. Diez, M.P. Gamasa, J. Gimeno, M. Manfranchi, A. Tiripicchio, J. Chem. Soc., Dalton Trans. (1990) 1027;
(f) J. Diez, M.P. Gamasa, J. Gimeno, A. Tiripicchio, M. Tiripicchio, J. Chem. Soc., Dalton Trans. (1987) 1275;
(g) A.M. Manotti Lanfredi, F. Ugozzoli, A. Camus, N. Marsich, Inorg. Chim. Acta 99 (1985) 111.
[20] (a) W. Tan, H. Zheng, Q. Jin, G. Jin, W. Ji, D. Long, X. Xin, Polyhedron 19 (2000) 1545;
(b) D. Li, H.-K. Yip, C.-M. Che, Z.-Y. Zhou, T.C.W. Mak, S.-T. Liu, J. Chem. Soc., Dalton Trans. (1992) 2445.
[21] (a) O. Fuhr, L. Fernandez-Recio, A. Castiñeiras, D. Fenske, Z. Anorg. Allg. Chem. 633 (2007) 700;
(b) P.C. Ford, E. Cariati, J. Bourassa, Chem. Rev. 99 (1999) 3625;
(c) T.A. Annan, R. Kumar, D.G. Tuck, J. Chem. Soc., Chem. Commun. (1988) 446.
[22] (a) M. Dennehy, O.V. Quinzani, R.M. Ferullo, S.D. Mandolesi, N. Castellani, M. Jennings, Polyhedron 27 (2008) 2243;
(b) M. Dennehy, S.D. Mandolesi, O.V. Quinzani, M. Jennings, Z. Anorg. Allg. Chem. 633 (2007) 2746;
(c) D.R. Pérez, S.H. Tarulli, O.V. Quinzani, J. Dristas, R. Faccio, L. Suescun, A. Mombrú, Z. Anorg. Allg. Chem. 633 (2007) 1066;
(d) M. Dennehy, O.V. Quinzani, M. Jennings, J. Mol. Struct. 841 (2007) 110;
(e) S.H. Tarulli, O.V. Quinzani, O.E. Piro, E.E. Castellano, E.J. Baran, J. Mol. Struct. 797 (2006) 56.
[23] Enraf-Nonius. COLLECT. Nonius BV, Delft, The Netherlands, 1997–2000.
[24] Z. Otwinowski, W. Minor, in: C.W. Carter Jr., R.M. Sweet (Eds.), Methods in Enzymology, vol. 276, Academic Press, New York, 1997, pp. 307–326.
[25] PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, A.L. Spek, 1998.
[26] G.M. Sheldrick, SHELXS-97, Program for Crystal Structure Resolution, University of Göttingen, Göttingen, Germany, 1997.
[27] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Analysis, University of Göttingen, Göttingen, Germany, 1997.
[28] C.K. Johnson, ORTEP-II. A Fortran Thermal-Ellipsoid Plot Program. Report ORNL-5318, Oak Ridge National Laboratory, TN, USA, 1976.
[29] O. Grupče, M. Penavić, G. Jovanovski, J. Chem. Crystallogr. 24 (1994) 581.
[30] (a) G. Jovanovski, A. Cahil, O. Grupče, L. Pejov, J. Mol. Struct. 784 (2006) 7;
(b) M.M. Branda, N.J. Castellani, S.H. Tarulli, O.V. Quinzani, E.J. Baran, R.H. Contreras, Int. J. Quant. Chem. 89 (2002) 525;
(c) Y.I. Binev, C. Petkov, L. Pejov, Spectrochim. Acta Part A 56 (2000) 1949.
[31] A. Bondi, J. Phys. Chem. 68 (1964) 441.
[32] (a) W. Wei, D. Di, W. Chu, Q. Zhu, R. Huang, Inorg. Chim. Acta 361 (2008) 1819;
(b) M. Dennehy, O.V. Quinzani, R.A. Burrow, Acta Cryst. Sect. C 63 (2007) m395.
[33] M. Dennehy, O.V. Quinzani, S.D. Mandolesi, J. Guida, G.A. Echeverría, O.E. Piro, Monatshefte Chem. 138 (2007) 669.
[34] (a) R. Pikl, F. Dushek, C. Fickert, R. Finsterer, W. Kiefer, Vib. Spectrosc. 14 (1997) 189;
(b) R.J.H. Clark, C.D. Flint, A.J. Hempleman, Spectrochim. Acta 43A (1987) 805;
(c) R.G. Inskeep, J. Inorg. Nucl. Chem. 24 (1962) 763.
[35] C. Kutal, Coord. Chem. Rev. 99 (1990) 213.
[36] M. Petiau, J. Fabian, J. Mol. Struct. Theochem. 538 (2001) 253.