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Unusual silver coordination by mono-carboxylate utilization of a poly-carboxylate anion, solid-state structures of silver-tetrachlorophthalate with phthalazine and amine ligands

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Abstract

Silver carboxylate coordination with the tetrachlorophthalate anion, in combination with neutral donor ligands, has been found to deviate from other known poly-carboxylate complexes. Both complexes reported here, bis-[tetrachlorophthalato-silver phthalazine] and bis-[ammino-tetrachlorophthato-silver di-ammino-silver], utilize mixed carboxylate bonding types for silver coordination. In the case of the phthalazine ligand, both chelating and monodentate carboxylates form the framework for the oligomeric structure. In the case of the ammine ligand, one carboxylate forms a monodentate connection to a silver-ammine group, while the other is simply involved with hydrogen bonding to lock in a $[(Ag–NH_3)_2–Ag–NH_3]$ substructure with an adjacent tetrachlorophthalato-silver unit. Both structures exhibit supramolecular connections *via* hydrogen bonding and π–π interactions.

Keywords: Silver complexes; Mono-carboxylate; Phthalate; Structure; Polymer; Dimer; X-ray crystal structures

1. Introduction

Many silver carboxylates have been structurally well characterized [1]. In nearly all of these cases, the silver adopts an eight-membered ring configuration that is polymerized by additional, long Ag–O bonding contacts with neighboring units. In addition, one of the most interesting features in these complexes is the Ag–Ag separation, which is typically found to be 2.8–3.0 Å. This distance encompasses the normal bond distance for metallic silver, 2.889 Å, and suggests metal–metal bonding interactions are likely present.

Silver carboxylate complexes containing neutral donor ligands completely change the polymeric structural units, including the Ag–Ag separation distance. For example, aromatic amine ligands, such as phthalazine (PHZ, Fig. 1), have been reported to form rearranged coordination polymers based on a silver-containing ring, $[AgPHZ_2{}^{2+}]$ dimer units in $[Ag(PHZ)PHZ(NO_3)]_2$ [2], and the same dimer in silver carboxylate complexes $[(Ag(PHZ))_{1\text{-}2}(carboxylate)]$ [3]. In these latter cases, the PHZ ligand dominates the structural motif, while the carboxylate anions remain partially coordinated to the silver by bridging the six-membered ring dimers. Changing to simpler ammine ligands, such as ammonia, enables many silver carboxylate complexes to crystallize well enough for solid-state structure characterization, previously inhibited by their generally poor solubility [4]. Approximately half of the structures reported from using this labile-volatile ligand approach incorporate the ammine into the structure well enough that it remains part of the complex to fill out the silver coordination sphere [5]. In our continuing efforts to further understand silver coordination chemistry [1d,1e,1f,3], we now report the contrasting cases of two quite different silver

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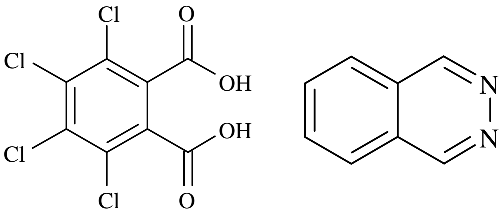

Fig. 1. TCPA, PHZ.

carboxylate complexes, resulting from the reaction of di-silver-tetrachlorophthalate (from tetrachlorophthalic acid, Fig. 1) with neutral donor ligands. Unlike the usual structures, when PHZ is the neutral donor, the complex does not polymerize by carboxylate bridging, and forms a bis-[tetrachlorophthalato-silver phthalazine] complex (**1**). With the NH_3 ligand, an unusual mixed structure of bis-[ammino-tetrachlorophthalato-silver di-ammino-silver] (**2**), results. In **1**, monomeric complexes are formed, and in **2**, the ammine is incorporated into the complex both as a route to fill out the silver coordination sphere and also in a way that incorporates $Ag(NH_3)_2^+$ units held together by N–H···O hydrogen bonds. This latter structure arrangement is not unusual for other anionic silver ammine complexes [6].

We report here the preparation and X-ray structure characterization of two unusual silver complexes constructed from these nitrogen-based ligands, which exhibit deviations in the anticipated structures relative to those previously reported. The phthalazine complex, $[AgPHZ \cdot HTCPA]_2(H_2O)_2$, is a stable complex having a silver coordination sphere similar to other known silver phthalazine carboxylate complexes but differs by virtue of its single carboxylate-coordination participation. The second, $[Ag(NH_3)_2Ag(NH_3)TCPA]$, also is limited to one of the carboxylates in the silver coordination sphere by incorporating the $Ag(NH_3)_2^+$ moiety *via* hydrogen bonding. The unusual bonding configuration resulting from these ligands may be useful for designing new silver-based materials.

2. Experimental

Preparation of **1**: $[AgPHZ \cdot HTCPA]_2(H_2O)_2$: To 0.13 g Ag_2TCPA (previously prepared from a stoichiometric reaction of $AgNO_3$ and Na_2TCPA in water) in a 4 oz bottle was placed a 0.5 oz bottle containing 45 mg PHZ. Water was added to both bottles until the top of the inner bottle was just covered. The large bottle was sealed, and the reagents were allowed to stand undisturbed for two weeks. Colorless needles grew on the outside of the inner bottle, which were collected and air dried.

Preparation of **2**: $[Ag(NH_3)_2Ag(NH_3)TCPA]_2(H_2O)_2$: To 1.7 g Ag_2TCPA was added 5 g H_2O, followed by concentrated NH_4OH dropwise until a clear solution was obtained. A slight discoloration was removed by filtering through 1.6 μm glass fiber filter paper, and the filtrate was allowed open to the atmosphere to slowly lose NH_3. A colorless, crystalline solid was obtained, which was decanted and air dried.

Single-crystal diffraction data were collected at 298 K using Nonius Kappa CCD [7]. Data reductions were performed using Denzo-SMN [8]. The unit cells for **1** and **2** were determined to be monoclinic, and the space groups were uniquely determined from systematic absences to be $P2_1/c$. The structure of **2** was solved by direct methods using Bruker SHELXTL [9] and that of **1** by using the "dual-space recycling method" in the XM [10] module of the Bruker SHELXTL [9] package. Both structures were refined by full-matrix, least-squares on F^2 with anisotropic displacement parameters for the non-hydrogen atoms using Bruker SHELXTL [9]. Hydrogen atoms were included in idealized positions with isotropic displacement parameters. The structures refined to final residuals of $R_1 = 0.0496$ and 0.0516 for **1** and **2**, respectively. The *R*-value (0.1593) for all data in **2** is high, which we attribute to a large amount of weak data, since out of 3665 observed reflections only 1705 are $>2\sigma$. In the structure of **1**, there are three molecules of $AgPHZ \cdot HTCPA$ in the asymmetric unit and two water molecules of solvation in the lattice. Three of the carboxylic oxygen atoms in the **1** structure were disordered and were left isotropic. Details of cell data, data collection, and structure refinement are summarized in Table 1.

3. Results and discussion

3.1. bis-[Tetrachlorophthalato-silver phthalazine] di-hydrate

The silver complex containing both phthalazine and TCPA, having the molecular formula $[AgPHZ \cdot HTCPA]_2(H_2O)_2$, is a very stable, colorless, crystalline solid. Unlike most silver carboxylate complexes containing multiple carboxylate groups, the carboxylate coordination is non-symmetric, Figs. 2 and 3.

It can be seen that the fundamental coordination sphere consists of a six-membered N–N–Ag–N–N–Ag ring with normal Ag–N bond distances, Figs. 2 and 3.

This six-membered ring is typical for silver phthalazine complexes [2,3]. In addition, it is notable that a simple, mono-dentate TCPA is bound to the silver, with Ag–O bond distances, Table 2, ranging 2.23(2)–2.532(7) Å. Most silver carboxylates show additional bonding with the carbonyl of the carboxylate group. While the long Ag···O at 2.739(16) Å distance is not uncommonly long, the asymmetric arrangement of the carboxylate relative to the silver suggests that it is not participating in a chelating conformation. The net result of the silver connection points in this complex produces a network structure, Fig. 4.

Silver poly-carboxylate complexes reported in the literature are found with a silver ion associated with each carboxylate [3a,4b,4c,12]; the single exception is the structure for silver-maleate [4b]. The Ag···Ag distance in the six-membered ring of the $[AgPHZ \cdot HTCPA]_2(H_2O)_2$ title complex is 3.2417(9) Å, which is well outside the range normally reported for a Ag–Ag bond (2.8–3.0 Å [13]), even though it is within the Van der Waals radii of 3.44 Å [14]. It

Table 1
Crystal data and structure refinement

	Complex **1** [AgPHZ · HTCPA]$_3$(H_2O)$_2$	Complex **2** [Ag(NH_3)$_2$Ag(NH_3)TCPA]$_2$(H_2O)$_2$
Empirical formula	$C_{48}H_{18}Ag_3Cl_{12}N_6O_{14}$	$C_8H_9Ag_2Cl_4N_3O_5$
Formula weight	1651.69	584.72
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions		
a (Å)	18.9878(3)	8.9823(3)
b (Å)	8.10050(10)	27.2419(8)
c (Å)	36.1155(7)	7.0743(2)
β (°)	98.9130(10)	111.2920(10)
Volume (Å^3)	5487.87(15)	1612.89(8)
Z	4	4
D_{calc} (Mg/m^3)	1.999	2.408
Absorption coefficient (mm^{-1})	1.717	3.113
$F(000)$	3220	1120
Crystal size (mm^3)	0.25 × 0.10 × 0.10	0.40 × 0.17 × 0.05
Theta range for data collection (°)	3.03–22.47	3.31–27.49
Index ranges	$-20 \leqslant h \leqslant 20$, $-7 \leqslant k \leqslant 8$, $-37 \leqslant l \leqslant 38$	$-11 \leqslant h \leqslant 11$, $-35 \leqslant k \leqslant 35$, $-9 \leqslant 1 \leqslant 9$
Reflections collected	25029	17965
Independent reflections	6907 [$R_{int} = 0.0446$]	3665 [$R_{int} = 0.1300$]
Completeness to theta = 27.49°	96.5%	99.1%
Absorption correction	multiscan [11]	multiscan [11]
Refinement method	full-matrix, least-squares on F^2	full-matrix, least-squares on F^2
Data/restraints/parameters	6907/0/747	3665/0/203
Goodness-of-fit on F^2	1.055	0.927
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0496$, $wR_2 = 0.1470$	$R_1 = 0.0516$, $wR_2 = 0.1134$
R indices (all data)	$R_1 = 0.0833$, $wR_2 = 0.1730$	$R_1 = 0.1593$, $wR_2 = 0.1407$
Extinction coefficient		0.0012(2)
Largest diffraction peak and hole (e Å^{-3})	0.815 and −0.696	1.088 and −1.103

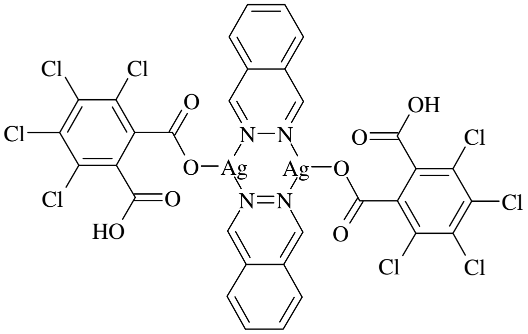

Fig. 2. Molecular structure of [AgPHZ · HTCPA]$_2$(H_2O)$_2$ (lattice H_2O not shown).

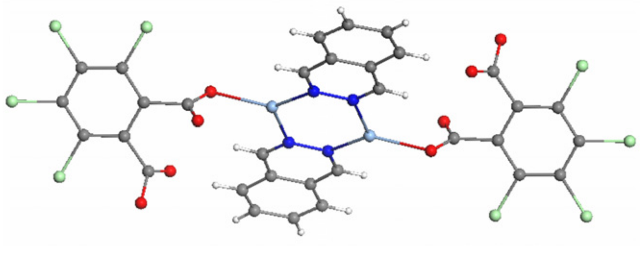

Fig. 3. Bonding pattern in [AgPHZ · HTCPA]$_2$(H_2O)$_2$.

is noteworthy that this structure also contains hydrogen bonding between the HTCPA and the lattice water (for example, O14–O2 and O13–O1 at 2.622 Å and 2.682 Å, respectively).

Table 2
Comparison of selected Ag–N, Ag–O, and Ag–Ag distances in AgTCPA complexes

[AgPHZ · HTCPA]$_2$(H_2O)$_2$		[Ag(NH_3)$_2$Ag(NH_3)TCPA]$_2$(H_2O)$_2$	
Ag(1)–N(5)	2.216(6)	Ag(1)–N(1)	2.119(6)
Ag(1)–N(6)	2.337(6)	Ag(1)–N(2)	2.125(6)
Ag(2)–N(1)	2.284(6)	Ag(2)–N(3)	2.150(5)
Ag(2)–N(4)	2.308(6)		
Ag(3)–N(2)	2.205(6)		
Ag(3)–N(3)	2.252(6)		
Ag(2)–O(8′)#1	2.23(2)	Ag(2)–O(2)	2.173(4)
Ag(2)–O(8)#1	2.367(16)		
Ag(2)–O(5)	2.390(6)		
Ag(3)–O(4)	2.462(7)		
Ag(3)–O(3)	2.532(7)		
Ag(1)–O(12)	2.331(6)		
Ag(2)–Ag(3)	3.2417(9)	Ag(2)–Ag(2)#1	3.1578(12)
		Ag(2)–Ag(1)#1	3.2757(8)
		Ag(1)–Ag(2)	3.3657(9)

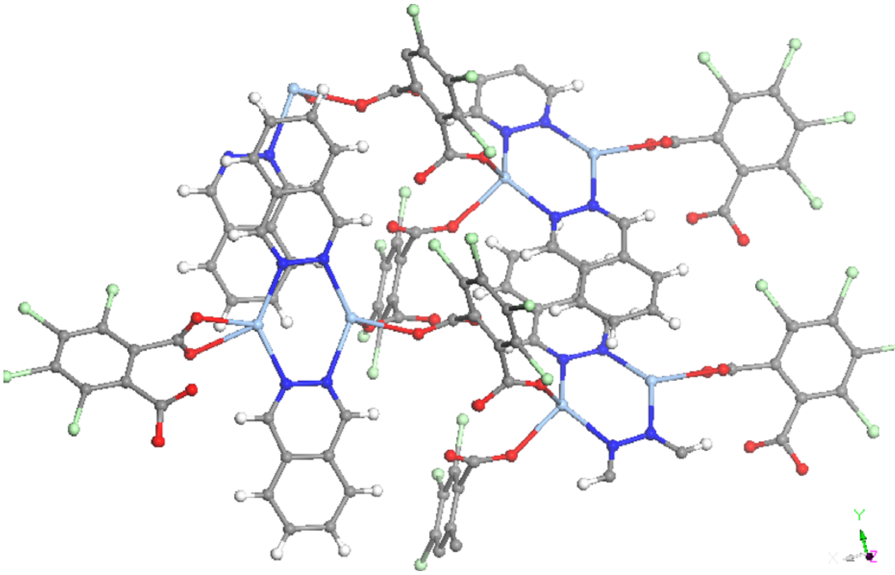

Fig. 4. Network connections in $[AgPHZ \cdot HTCPA]_2(H_2O)_2$.

Ordinarily, this dimeric complex, despite its high molecular weight, might be expected to exhibit some water solubility. However, extensive π–π interactions between the aromatic rings of the PHZ and TCPA, and especially between PHZ and PHZ at 3.307 Å, are well within the normal range observed for these types of interactions in the literature [15].

3.2. bis-[Ammino-tetrachlorophthato-silver di-ammino-silver] di-hydrate

Silver carboxylates typically exhibit poor solubility [16], which inhibits the preparation of crystals suitable for single-crystal X-ray structure analysis. One approach to enhance the prospects of forming single crystals is slow crystallization of the water-soluble ammine complex as a result of the ammine equilibrium evolving free, volatile ammonia [4]. That is, an equilibrium is established that takes advantage of the reversible dissociation of the NH_3 ligand and its volatility:

$$\begin{aligned}(NH_3)_2Ag(O_2CR)(aq) &\leftrightarrow (NH_3)Ag(O_2CR)(aq) \\ &\quad + NH_3(g) \\ &\leftrightarrow Ag(O_2CR)(s) + NH_3(g) \qquad (1)\end{aligned}$$

Under these circumstances, the ammine may be completely eliminated from the silver coordination sphere [4], but often times it is retained as part of the isolated complex [5]. In the case of Ag_2TCPA, when recrystallized from NH_3, the ammine ligand is retained in the structure. What is unique, however, is how the ammine is incorporated in this case to form a bis-[ammino-tetrachlorophthalato-silver di-ammino-silver] complex. That is, this unusual complex consists of a combination of two completely different silver structures – that of a diammine silver group superimposed on an ammino-silver carboxylate framework. The structure is shown schematically in Fig. 5 and as an Ortep drawing in Fig. 6.

The two different silver ammine units are connected together *via* extensive hydrogen bonding into a cubic core capped with TCPA ligands, Fig. 7.

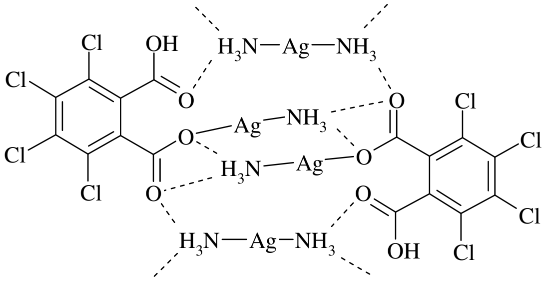

Fig. 5. Molecular structure of $[Ag(NH_3)_2Ag(NH_3)TCPA]_2(H_2O)_2$ (lattice water not shown).

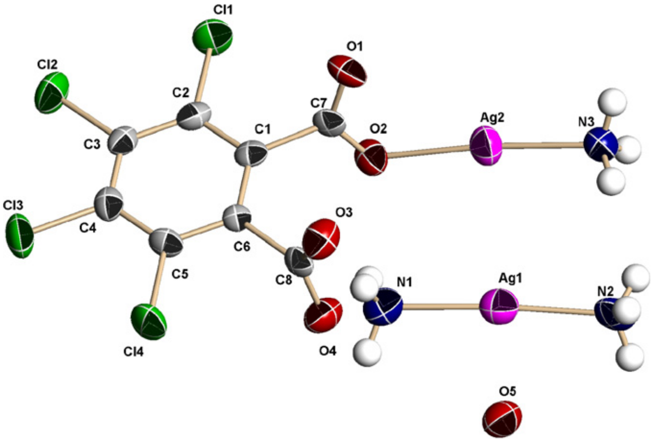

Fig. 6. Formula unit of $[Ag(NH_3)_2Ag(NH_3)TCPA]_2 \cdot (H_2O)_2$.

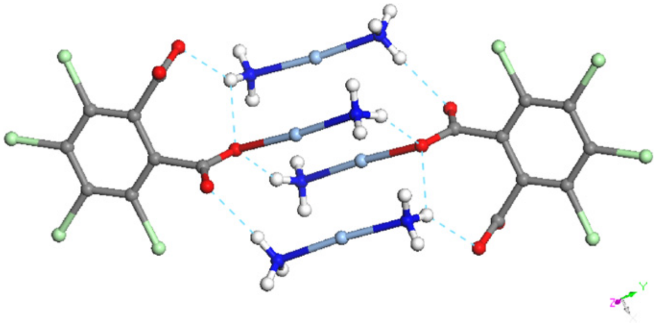

Fig. 7. Silver ammine connections in $[Ag(NH_3)_2Ag(NH_3)TCPA]_2 \cdot H_2O_2$.

The two distinct silver coordination spheres can be treated independently for discussion purposes. The simplest component, $Ag(NH_3)_2^+$, is a two coordinate, nearly linearly bound silver, which is quite normal when compared to the other $Ag(NH_3)_2^+$ (X^-) structures reported in the literature [6]. In these cases, X^- is NO_3^-, NO_2^-, and SO_4^{2-}, all produce the same linear structure in the $Ag(NH_3)_2^+$ unit and with only small crystal lattice differences when changing the anion. The solid-state structure of these complexes is the result of extended N–H···O bonding, which connects the $Ag(NH_3)_2^+$ units into an extended structure. The hydrogen bonding in these complexes range 2.971(4)–3.0229(4) Å, where normal N–H···O distances of 2.78–3.13 Å have been reported [6]. It is clear that the same connectivity is occurring in the title complex $[Ag(NH_3)_2Ag(NH_3)TCPA]_2(H_2O)_2$ structure, where the N–H···O distances range 2.937–3.427 Å, Table 3.

While the silver atoms are stacked over each other in **2** that give the appearance of argentophilic bonding, the Ag–Ag separations, 3.143–3.366 Å, are quite outside the normal bonding range for accepted Ag–Ag bonds, 2.78–3.0 Å [13]. From a physical properties perspective, it is noteworthy that the $X^- = NO_3^-, NO_2^-$, and SO_4^{2-} complexes are all unstable as the result of NH_3 loss from the solid, beginning within just a few hours, in some cases. The bis-[ammino-tetrachlorophthalato-silver di-ammino-silver] complex reported here, on the other hand, is surprisingly stable and the di-ammine-silver group is retained intact.

Table 3
N–H···O bonding in $[Ag(NH_3)_2Ag(NH_3)TCPA]_2(H_2O)_2$, d(D–H) = 0.890

D–H	d(H...A)	∠DHA	d(D...A)	A
N1–H1A	2.320	153.82	3.144	O3
N1–H1B	2.353	132.73	3.028	O1
N1–H1C	2.243	144.01	3.009	O4
N1–H1C	2.434	121.51	2.997	O2
N2–H2A	2.143	151.75	2.957	O3
N2–H2B	2.440	150.01	3.242	O1
N2–H2C	2.225	164.77	3.092	O4
N3–H3A	2.515	152.62	3.331	O4
N3–H3A	2.642	147.66	3.427	O3
N3–H3B	2.111	176.27	3.000	O1
N3–H3C	2.284	153.52	3.106	O2

The second component of **2**, the ammino-silver tetrachlorophthalate, is very reminiscent of $[NH_3AgCBBA]$ [5c], where CBBA is 2-(4-chloro-benzoyl)-benzoic acid. In that case, a simple mono-silver-carboxylate structure is observed that is analogous to the TCPA component of the title complex. The 2.119(6)–2.150(5) Å Ag–N bond lengths compare well to the two-coordinate silver in the $[NH_3AgCBBA]$ complex, 2.098(2) Å. In the literature, the only relevant $Ag–N_{ammine}$ bond distances are 2.158(5) Å for a 2,3-pyrazinedicarboxylato-di-silver(I) ammine complex [4c] and 2.154(5) Å for the *p*-nitrobenzoato-silver(I) ammine complex [5a]. Simple $[Ag(NH_3)_2]^+$ complexes, on the other hand, exhibit $Ag–N_{ammine}$ bond lengths of 2.11–2.18 Å [6d,6e]. The carboxylate functionality in **2** shows the Ag–O bond to be a robust 2.173(4) Å, compared to the $[NH_3AgCBBA]$ complex, where these bonds are normal but significantly longer at 2.309(2) and 2.468(2) Å. The shorter bond length for **2** is expected for a stable Ag–O bond, and the longer Ag–O bond is not unusual, which range up to 2.7 Å [1,4].

There is one more significant point that is worth mentioning regarding **2**. In order to achieve charge balance, both carboxylates of the TCPA group must be anionic, not just the one involved with silver coordination. As a result, each of the $Ag(NH_3)_2^+$ groups, which have no significant Ag–O contact distances, is held in place by N–H bonding with a CO_2^-, while the remaining $Ag(NH_3)^+$ is bound to the second CO_2^-. This hydrogen bonding provides both charge balance as well as a second ligand for the silver's coordination sphere. Presumably, it is this linkage that provides the anchor stability to the solid-state structure that prevents NH_3 loss so common to the other anion versions [6].

Appendix A. Supplementary material

CCDC 654180 and 654181 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.08.031.

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