Synthesis, thermal analysis and crystal structure of lead(II) diaqua 3,6-dicarboxylatopyridazine. Evaluation of performance as a synthetic precursor†

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$Pb(H_2O)_2DCP$ (DCP = 3,6-dicarboxylatopyridazine) has been synthesized and characterized by thermal gravimetric analysis and single crystal X-ray dffraction: tetragonal, space group $I4_1/a$, $a = b = 15.278(2)$, $c = 15.218(3)$ Å, $U = 3552.3(1)$ Å^3, $Z = 16$. The structure consists of columns of lead atoms linked by tetradentate DCP molecules in a spiral array. The irregular 8-fold coordination sphere of Pb^{II} consists of two bidentate DCP molecules, the oxygen atoms of two neighboring ligands and two coordinated water molecules. The thermal decomposition of this complex to yield PbO at low temperatures was observed by powder diffraction and by thermal gravimetric analysis. Comparison of $Pb(H_2O)_2(DCP)$ and $Pb(H_2O)_2(oxalate)$ as precursors in the synthesis of the mixed metal oxide, $Bi_{12}PbO_{19}$, showed the use of $Pb(H_2O)_2(DCP)$ to result in mixed metal oxide product with a smaller grain size.

Synthèse, etude thermique et structure cristalline du plomb(II) diaqua 3,6-dicarboxylatopyridazine. Utilisation potentielle en tant que précurseur de synthèse. Le composé plomb(II) diaqua 3,6-dicarboxylatopyridazine [$Pb(H_2O)_2DCP$] a été préparé puis étudié par analyse thermogravimètrique. La structure cristalline à été déterminée par diffraction des rayons X sur monocristal; le système cristallin est quadratique, groupe d'espace $I4_1/a$, avec $a = b = 15.278(2)$, $c = 15.218(3)$ Å, $U = 3552.3(1)$ Å^3, $Z = 16$. Le modèle structural est bâti à partir de colonnes d'atomes de Pb, reliées par deux ligands tétradentate de DCP et développées en spirales. La coordinance huit du plomb(II) est obtenue à partir de deux ligands DCP bidentates, de deux atomes d'oxygène provenant de deux ligands voisins et de deux molécules d'eau. L'évolution thermique de ce complexe a été suive par thermodiffraction X et analyse thermogravimètrique. Elle conduit à l'obtention de PbO dès 275 °C. Un test comparatif d'utilisation des complexes oxalates ou DCP pour la synthèse de $Bi_{12}PbO_{19}$ a prouvé l'intérêt de ce dernier, qui conduit à l'obtention de l'oxide mixte avec une faible granulométrie.

Interest in the use of organometallic complexes as potential precursors of the metal oxides necessary for further synthesis of conducting or superconducting materials by low temperature or "chimie douce" procedures has increased in recent years. The most widely used complexing agents are tartaric acid,[1,2] EDTA (ethylenediaminetetraacetic acid),[3,4] oxalic or acetic acid,[5–9] and also precursors such as β-diketonates.[10,11] Subsequent pyrolysis yields finely divided oxide powders at relatively low temperatures. However, the grain size of these precursors has proved to be linked to the conductivity of potentially superconducting products. Large grain sizes of the metal oxides lead to inhomogeneities within the final product and to diminished conductivity. Thus, there is interest in exploration of other ligand systems whose thermal decomposition may lead to more finely divided metal oxides. DCP (3,6-dicarboxylatopyridazine) is a tetradentate ligand that can be used as a precipitating reagent for a wide variety of elements.[12] Indeed, we have recently reported the preparation and structures of $Cu_2(H_2O)_2DCP$ and $Fe_2(H_2O)_2DCP$ dihydrate[13] and $Cu(H_2O)_2DCP$ dihydrate.[14] The structures of Pb(oxalate) dihydrate[15] and Pb(oxalate) trihydrate[16] have also been reported. We report here the preparation and structure of a new complex, $Pb(H_2O)_2(DCP)$, the evaluation of its degradation process by thermal gravimetric analysis and a comparison, with that of $Pb(H_2O)_2(oxalate)$, of its performance in the preparation of a mixed metal oxide.

Experimental

Synthesis

A solution of 0.66 g (2 mmol) of $Pb(NO_3)_2$ in 10 ml of 2 N aqueous nitric acid and a solution of 0.4 g (2.2 mmol) of 3,6-dicarboxypyridazine monohydrate[17] ($3,6\text{-}H_2DCP \cdot H_2O$) in 10 ml of 2 N aqueous nitric acid were mixed together under stirring, thus producing a white precipitate. The mixture was maintained at room temperature for 1 h. The precipitate was filtered off, washed successively with hot water and diethyl ether. As a result of thermogravimetric analysis, the collected compound can be formulated as $Pb(H_2O)_2DCP$,

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† *Supplementary material available:* infrared spectra of DCP and $Pb(H_2O)_2DCP$. Available from BLDSC (No. SUP 57493, 4 pp.) See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/njc).

Table 1 Crystal data for $Pb(H_2O)_2DCP$

Formula	$C_6H_6N_2O_6Pb$
M	409.32
Space group	$I4_1/a$
$a = b$/Å	15.278(2)
c/Å	15.218(3)
α, β, γ/°	90.0
U/Å^3	3552(1)
Z	16
D_{meas}/g cm^{-3}	3.03(1)
D_{calc}/g cm^{-3}	3.062
$F(000)$	2976
Crystal dim./mm	0.044 × 0.044 × 0.33
μ(MoK$_\alpha$)/mm^{-1}	19.011
λ(MoK$_\alpha$)/Å	0.71069
$R_{\mathrm{(int)}}$	0.0561
Param. refined	137
R, wR	0.0357, 0.0549
Ext. coef.	0.00048(3)
Ext. exp. (x)	$F_c^* = kF_c[1 + 0.001xF_c^2\lambda^3/\sin(2\theta)]^{-1/4}$
Reflns. meas.	4892
Reflns. [$I > 2\sigma(I)$]	1316
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0163P)^2 + 16.9366P]$ where $P = (F_o^2 + 2F_c^2)/3$
h, k, l	−14, to 17; −14 to 18; −18 to 14
θ range/°	2.67–25.09

yield: 96%. The compound is insoluble in most usual organic solvents.

Thermal analysis

Thermal gravimetric analysis was carried out on a 951 Dupont thermobalance coupled to a 1090B thermal analyzer and using either 30 or 60 °C/h as the heating rate. X-Ray data were measured using monochromated CuK$_\alpha$($\lambda = 1.541\,78$ Å) radiation and a Guinier–De Wolff camera (room temperature) or a Guinier–Lenné moving film camera (high temperature, 40 h exposure, film speed 2 mm h^{-1}).

Single crystal X-ray diffraction

A needle-shaped single crystal of $Pb(H_2O)_2DCP$ was obtained by slow evaporation of a solution of the corresponding powder in nitric acid. Data collection was accomplished using a Nonius CAD4 equipped with monochromated MoK$_\alpha$ radiation at room temperature. The resulting data were corrected for Lorentz, polarization, background and absorption effects.

The choice of a space group presented problems. The unit cell dimensions allowed a choice between tetragonal [$I4_1/a$, $Z = 16$, $U = 3552(1)$ Å^3, asymmetric unit = $Pb(H_2O)_2DCP$], monoclinic {non-standard space groups $I2_1/c = I2/a$, $Z = 8$, $U = 3552(1)$ Å^3, asymmetric unit = [$Pb(H_2O)_2DCP$]$_2$}, or triclinic {$P\bar{1}$, $Z = 4$, $U = 1776.1$ Å^3, asymmetric unit = [$Pb(H_2O)_2DCP$]$_2$} space groups. While the structure was originally solved in the triclinic $P\bar{1}$, and later in the monoclinic and tetragonal groups, the pseudo symmetry between the two Pb atoms in the groups of lower symmetry is incorporated into the space group symmetry of $I4_1/a$. Furthermore, the l absence, $l = 4n$, which was apparent in the data, is required only in that space group. Thus, the crystallographic results in space group $I4_1/a$ are reported. Solution and refinement (SHELXS,[18] SHELXL[19]) converged to a final R factor of 3.57% (Table 1). Selected bond angles and distances, based on the final positional parameters, are given in Table 2.

Table 2 Selected bond distances (Å) and angles (°) for $Pb(H_2O)_2DCP$

Pb1—O3	2.532(6)	Pb1—O1‴	2.668(6)
Pb1—O1′	2.558(6)	Pb1—N2′	2.675(7)
Pb1—N3	2.651(7)	Pb1—O31	2.694(7)
Pb1—O3″	2.664(6)	Pb1—O32	2.781(7)
O3—Pb1—O1′	112.22(19)	O1′—Pb1—N2′	60.5(2)
O3—Pb1—N3	61.6(2)	N3—Pb1—N2′	85.7(2)
O1′—Pb1—N3	71.1(2)	O3″—Pb1—N2′	138.48(19)
O3—Pb1—O3″	121.78(15)	O1‴—Pb1—N2′	71.48(19)
O1′—Pb1—O3″	79.30(17)	O3—Pb1—O31	76.7(2)
N3—Pb1—O3″	70.7(2)	O1′—Pb1—O31	153.2(2)
O3—Pb1—O1‴	79.68(18)	N3—Pb1—O31	93.6(2)
O1′—Pb1—O1‴	119.90(15)	O3″—Pb1—O31	74.8(2)
N3—Pb1—O1‴	140.1(2)	O1‴—Pb1—O31	86.0(2)
O3″—Pb1—O1‴	145.51(18)	N2′—Pb1—O31	142.3(2)
O3—Pb1—N2′	69.9(2)		

Symmetry operations ′:y, $-x + 1/2$, $z + 1/4$. ″:$-y + 1/2$, x, $z - 1/4$. ‴: $-x + 1/2$, $-y + 1/2$, $z + 1/2$.

CCDC reference number 440/097. See http://www.rsc.org/suppdata/nj/1999/393/ for crystallographic files in .cif format.

Results and discussion

Thermal analysis

The compound formulation $Pb(H_2O)_2(DCP)$ results from thermal gravimetric analysis (anal. Pb: 0.957; H_2O 1.95; DCP: 0.974). The TGA scan (Fig. 1) clearly indicates successive weight losses leading to a final residue identified as pure PbO. If the heating rate is rapid (60 °C/h), one sees a single step at 50 °C corresponding to the loss of two moles of water (1.95 exp.; 8.5% of the initial sample weight) per mole of PbDCP. With a slower heating rate (30 °C/h), dehydration of the initial organometallic complex proceeds in two steps; the first at 40 °C is equivalent to the loss of 1.5 H_2O per molecular formula and a second one at 60 °C, corresponds to the loss of 0.5 mole of water. Between 230 and 390 °C, the ligand decomposes and a loss of about 1 mole of DCP per Pb atom (exp. 0.974 mole) is seen.

Analysis of the powder diffraction spectrum measured at increasing temperatures allows a more detailed analysis. Between room temperature and 40 °C, the pattern is typical of the starting sample, which can be formulated as $Pb(H_2O)_2(DCP)$. Between 40 and 60 °C, a different pattern is observed. According to the TGA, this pattern must correspond to $Pb(DCP)\cdot 0.5H_2O$. Above 60 °C further modification in the powder spectrum corresponds to the completely dehydrated material, Pb(DCP). At 390 °C, decomposition of the organic ligand yields a mixture of PbO (massicot,[20] yellow, orthorhombic) and PbO (litharge,[21] red, tetragonal). This mixture of lead oxides undergoes oxidation in air at 445 °C to yield the typical diffraction pattern of Pb_3O_4[22] [$Pb^{IV}Pb^{II}_2O_4$], which disappears at 530 °C, leaving the diffraction pattern of pure PbO (massicot form).

However, observation of the evolution of the powder pattern under more controlled conditions reveals the existence of an additional phase between the mixture of massicot and

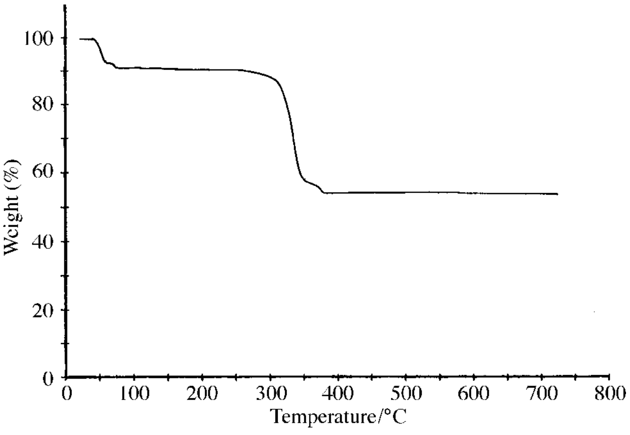

Fig. 1 TGA scan of $Pb(H_2O)_2(DCP)$.

litharge phases and the oxidized product, Pb_3O_4. High temperature powder diffraction, that is heating from 200 to 300 °C over a ten-hour period, followed by 30 h at 300 °C, shows the formation of PbO (both massicot and litharge forms) at temperatures as low as 270 °C. Then, after 5 h at 300 °C in air, PbO undergoes oxidation to give $PbO_{1.44}$.[23]

Continual observation of the powder diffraction pattern of a sample heated directly at 300 °C (temperature at which decomposition of the ligand begins) for 10 h leads to the identification of $PbO_{1.44}$ as the solid residue at room temperature. The compound $PbO_{1.44-1.57}$ has also been noted in the thermal decomposition scheme of Pb oxalate.[24] The cubic unit cell dimensions reported there agree with those observed in this work.

The decomposition sequence observed for $PbO_{1.44}$ is in agreement with literature observations that the red, tetragonal form (litharge) is of greater thermodynamic stability than the yellow, orthorhombic (massicot) form. Literature reports also suggest that the yellow massicot form converts to the red form, which is then oxidized to Pb_3O_4.

Crystal structure

Columns of Pb atoms, [Pb···Pb separation, 3.994(4) Å] extend parallel to the *c* axis of the cell. The arrangement of Pb atoms is only approximately linear. Each Pb atom is bound to a nitrogen atom [Pb—N 2.651(7)–2.675(7) Å], to the *ortho* carboxylate oxygen atom [Pb—O 2.532(6)–2.668(6) Å] of two different ligand molecules, to the carboxylate oxygen atom of two additional organic molecules and to two water molecules [Pb—O, 2.694(7) and 2.781(7) Å] (Fig. 2). The geometry of the eight-fold coordination is irregular.

Each successive pair of lead atoms is bridged by a Pb—N—N—Pb link and by two bridging oxygen atoms. Carboxylate groups are coplanar with the aromatic ring (ligand dev: 0.045) and successive ligand planes subtend an interplanar angle of 87.7°.

A projection view of the structure (Fig. 3) shows the polymeric units packed in a parallel array without significant channels between columns. Columns are held in close proximity by networks of hydrogen bonds involving the water molecules.

Examination of the solid state structures of $Pb(H_2O)_2(DCP)$ and of the red and yellow forms of PbO and of Pb_3O_4 (the single crystal structure of $PbO_{1.44}$ is unreported) in an effort to discover a structural progression during decomposition was unfruitful.

Evaluation of performance as a synthetic precursor

Synthesis of $Bi_{12}PbO_{19}$. Stoichiometric quantities of Bi_2O_3 and PbO [$PbO/(PbO + Bi_2O_3) = 0.143$] were dissolved in a minimum volume of concentrated nitric acid to give the nitrates of the two metals. The pH of the solution was adjusted with an appropriate quantity of distilled water to pH 1.40. At the same time, the stoichiometric quantity of ligand (metal : ligand = 1 : 1, ligand = DCP) was dissolved in a minimum quantity of hot nitric acid. The two solutions were mixed and stirred for 12 h. On cooling, product appeared in the form of a white powder, which was dried using a rotary evaporator. The remaining material was then ground to a fine powder and dried in a dessicator under vacuum.

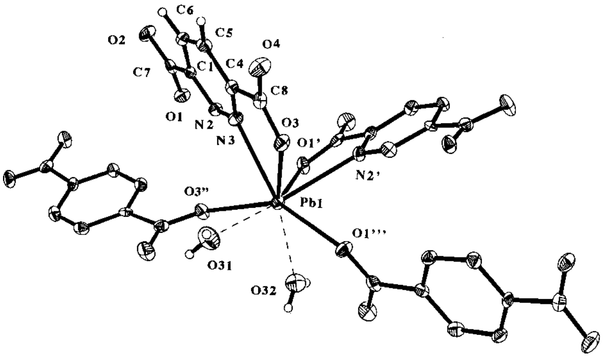

Fig. 2 View of the Pb coordination (′: $y, -x + 1/2, z + 1/4$; ″: $-y + 1/2, x, z - 1/4$; ‴: $-x + 1/2, -y + 1/2, z + 1/2$).

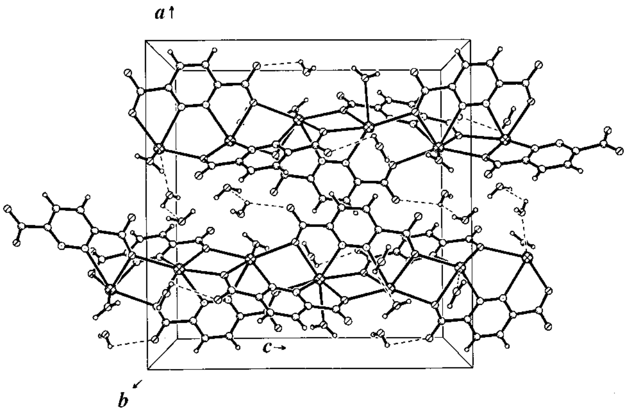

Fig. 3 Projection view of $Pb(H_2O)_2(DCP)$ on the 101 plane.

A similar preparation process was carried out using oxalic acid and the performance of the ligands was evaluated.

Thermal decomposition of mixed metal ligand complexes. The thermal decomposition of the mixed metal complexes leading to formation of $Bi_{12}PbO_{19}$ was followed both by TGA and by powder diffraction under changing thermal conditions. Both methods were in agreement on the progress of the decomposition.

The powder pattern of the bismuth–lead oxalate [Fig. 4(*a*)] shows a more complicated evolution in three steps: between room temperature and 335 °C dehydration and ligand decomposition take place; between 335 and 488 °C, tetragonal Bi_2O_3 is formed; at 488 °C (*i.e.* about 50 °C above the corresponding

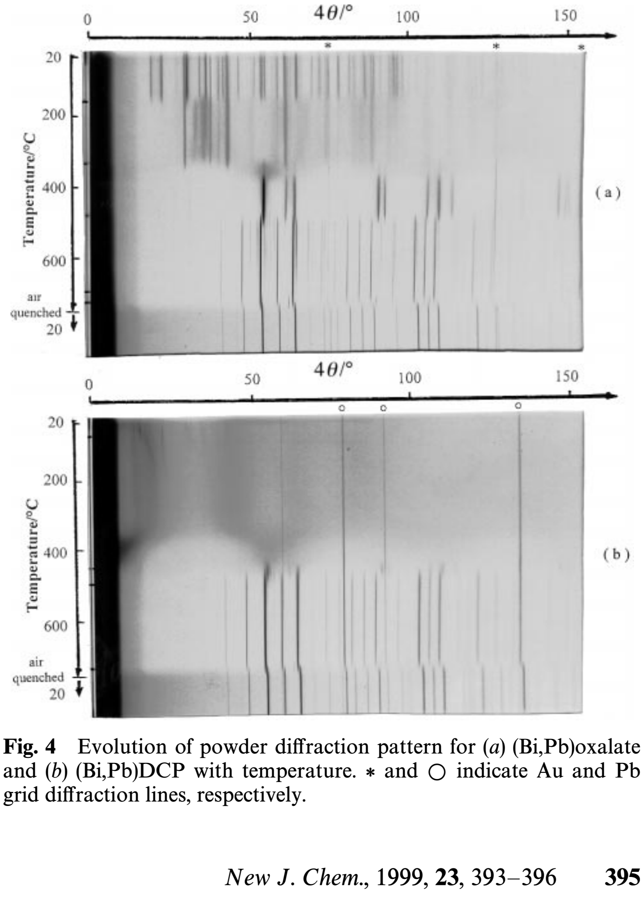

Fig. 4 Evolution of powder diffraction pattern for (*a*) (Bi,Pb)oxalate and (*b*) (Bi,Pb)DCP with temperature. * and ○ indicate Au and Pb grid diffraction lines, respectively.

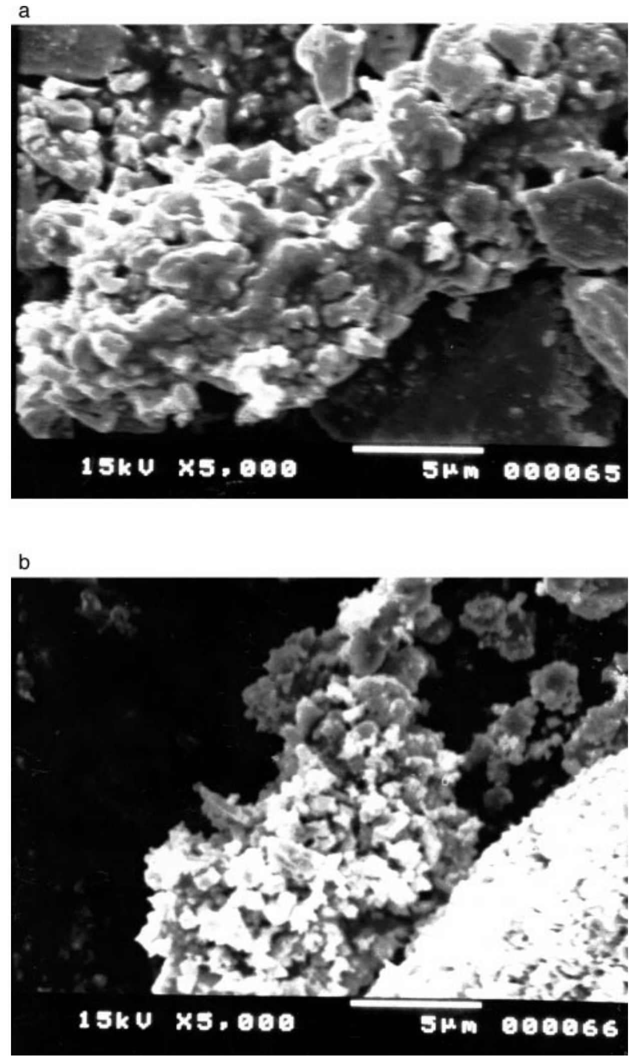

Fig. 5 Electron microscope photographs of $Bi_{12}PbO_{19}$ prepared from (*a*) oxalate and (*b*) DCP precursors.

temperature for the DCP compound) the sillenite type oxide, $Bi_{12}PbO_{19}$, is seen in the presence of Bi_2O_3.

The corresponding DCP complex undergoes a simpler decomposition process: ligand decomposition [Fig. 4(*b*)] occurs up to 443 °C; $Bi_{12}PbO_{19}$ appears along with Bi_2O_3 above that temperature.

Electron microscopy. The grain size of the products resulting from decomposition of (Bi,Pb)oxalate or (Bi,Pb)DCP was evaluated using a scanning electron microscope. In both cases the grain size was smaller than that observed for products prepared by solid state fusion methods. Moreover, the grain size was observed to be inversely related to the mass of the ligand. The $Bi_{12}PbO_{19}$ prepared using the oxalate precursor [Fig. 5(*a*)] displayed a larger grain size than that prepared using mixed metal DCP [Fig. 5(*b*)].

Conclusions

A new compound, lead(II) diaqua 3,6-dicarboxylatopyridazine, has been synthesized and structurally characterized by single crystal X-ray diffraction methods. The structure consists of polymeric chains of Pb atoms bridged in successive pairs by DCP molecules. These adopt a spiral conformation about the polymeric chain. The irregular coordination sphere of Pb is completed by coordination to two water molecules. Under dynamic conditions, thermal decomposition of the compound progresses *via* a mixture of the massicot and litharge forms of PbO, to Pb_3O_4, and finally shows complete conversion to the yellow or massicot form.

$Bi_{12}PbO_{19}$ prepared by thermal decomposition of precursor DCP complexes is seen to be prepared at lower temperatures and with a smaller grain size than that prepared by thermal decomposition of oxalate precursors. Thus, DCP is most promising as a precursor for synthesis of lead-based metal compounds.

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