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Crystal and molecular structures of the acetylacetonate derivatives $[Se(CH_3C(O)CC(O)CH_3)]_2$ and $[PhSe]_2[CH_3C(O)CC(O)CH_3]$

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Abstract

All attempts to synthesise Se^{IV} derivatives of acetylacetone resulted in the formation of Se^{II} complexes with the selenium atom coordinated to the methine carbon atom of the ligand. The crystal structure of $[Se(acac)]_2$ (where acac = $CH_3C(O)CC(O)CH_3$) shows a Se–Se separation of 2.9007(4) Å. $[PhSe]_2[acac]$ contains two independent molecules within the unit cell and steric restraints are less severe, so that the Se–Se separation is approximately 3.34 Å. Crystals of $[Se(acac)]_2$ are monoclinic, space group $P2_1/c$ with $Z = 2$, a 6.9979(9), b 7.881(2), c 10.843(2) Å and β 94.26(1)°. Crystals of $[PhSe]_2[acac]$ are triclinic, space group $P\bar{1}$, with $Z = 4$, a 9.796(2), b 10.675(1), c 17.162(2) Å, α 73.504(9), β 88.71(1), γ 74.00(1)°. For both complexes there is evidence for stereochemically active lone electron pairs on the Se atoms.

Introduction

Group 16 derivatives of β-diketones were first synthesised by Morgan and Drew in the early 1920s [1]. It was already clear then that such derivatives were not coordinated simply through the oxygen atoms of the acetylacetone ligand. The cyclic structure first proposed [1] for $[Se(acac)]_2$ (acac = $CH_3C(O)CC(O)CH_3$) has been supported by proton NMR and infrared spectroscopic studies [2]. This description of the complex appears in many texts but the crystal structure has not been reported previously.

Notable is the absence of any Se^{IV} acetylacetonate derivatives; in each case, attempts to prepare such compounds resulted in reduction of Se^{IV} to Se^{II} species.

However, diorganoselenium(IV) derivatives of β-diketones are known, and are ylides [3], with the selenium atom bonded to the methine carbon of the β-diketone. As part of our continuing interest in complexes of group 16 elements we have investigated reactions of β-diketones with selenium(IV) and selenium(II) and now report the structures of $[\mathrm{Se(acac)}]_2$ and $[\mathrm{PhSe}]_2[\mathrm{acac}]$.

Experimental

Synthesis

$[\mathrm{Se(acac)}]_2$: A solution of $\mathrm{SeCl_4}$ and Na(Hacac) (1/4 mole ratio) in dichloromethane was kept for 2 h. The NaCl precipitate then filtered off, and the solvent allowed to evaporate slowly to give pale yellow $[\mathrm{Se(acac)}]_2$, m.p. 183–185 °C (lit. [1(a)] 185 °C). (Analyses: Found: C, 33.60; H, 3.31. $\mathrm{C_5H_6O_2Se}$ calcd.: C, 33.86; H, 3.41%). Crystals suitable for X-ray analysis were obtained by slow evaporation of a solution in acetonitrile.

$[\mathrm{PhSe}]_2[\mathrm{acac}]$: Na(Hacac) was added to a solution of PhSeCl in dichloromethane and the mixture was stirred for 2 h. The solution was filtered and the solvent removed by evaporation. Addition of petroleum ether (b.p. 40–60 °C) caused precipitation of pale yellow crystals (m.p. 150–151 °C; (Analyses; Found: C, 48.74; H, 3.87. $\mathrm{C_{17}H_{16}O_2Se_2}$ calcd.: C, 49.77; H, 3.93%), some of which were suitable for X-ray analysis. Elemental analyses were performed by AMDEL, Victoria.

Crystallography

Crystals of both complexes were initially investigated by means of oscillation and Weissenberg photographic methods. Intensity data for both crystal structures were collected on an Enraf–Nonius CAD-4F diffractometer. Accurate cell dimensions were obtained from the setting angles of 25 reflections, measured using Mo-K_α (graphite-monochromator) radiation (λ 0.71069 Å), by a least squares procedure. Crystal data for the complexes are given in Table 1.

Details of the data collection below refer primarily to $[\mathrm{Se(acac)}]_2$, with the corresponding details for $[\mathrm{PhSe}]_2[\mathrm{acac}]$ in brackets. Intensity data were collected using the ω–2θ scan method to a maximum Bragg angle of 27.5° (25.5°), using Mo-K_α radiation. Three reflections, monitored every 4000 (4000) seconds X-ray exposure time, showed no significant (8%) decrease in intensity during the data collection. For $[\mathrm{PhSe}]_2[\mathrm{acac}]$ there was a significant variation and the data were corrected accordingly. For both crystals the data were corrected for Lorentz and polarization effects, but not for extinction. A total of 2564 (7235) reflections were measured, of which 1360 (6122) were unique, R_{amal} 0.018 (0.023), and 1181 (3471) were considered observed, $I \geq 2\sigma(I)$.

For $[\mathrm{Se(acac)}]_2$ the position of the selenium atom was located from a three-dimensional Patterson synthesis. For $[\mathrm{PhSe}]_2[\mathrm{acac}]$ the four unique selenium atoms were located from an E-map, generated by the SHELX-76 [4] direct methods subroutine EEES. The other non-hydrogen atoms of both structures were located from subsequent difference maps. Both structures were refined by a full-matrix least squares refinement procedure, with anisotropic temperature factors assigned to all atoms. All hydrogen atoms were located from the difference maps. For $[\mathrm{Se(acac)}]_2$ the positions of the hydrogen atoms were refined, while for $[\mathrm{PhSe}]_2[\mathrm{acac}]$ they were constrained at calculated positions with a C–H bond length of 1.08 Å. The

Table 1

Crystal data for $[Se(CH_3\text{-}C(O)CC(O)CH_3)]_2$ (1) and $[PhSe]_2[CH_3C(O)CC(O)CH_3]$ (2)

Compound	1	2
Formula	$C_{10}H_{12}O_4Se_2$	$C_{17}H_{16}O_2Se_2$
M	354.12	410.22
Crystal class	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
Z	2	4
Vol, Å^3	596.3	1651.1
a, Å	6.9979(9)	9.796(2)
b, Å	7.881(2)	10.675(1)
c, Å	10.843(2)	17.162(2)
α, deg.		73.504(9)
β, deg.	94.26(1)	88.71(1)
γ, deg.		74.00(1)
ρ(calc.) g cm^{-3}	1.972	1.650
ρ(meas) g cm^{-3}	1.96	1.650
No. unique reflections	1181	3471
Radiation	Mo-K_α (graphite monochromator) λ 0.71069 Å	
Crystal dimensions	$\pm(011)0.264$	$\pm(001)0.225$
	$\pm(0\bar{1}1)0.218$	$\pm(010)0.055$
	$(010)0.205$	$(\bar{1}00)0.200$
	$(0\bar{1}0)0.246$	$(102)0.130$
	$(00\bar{1})0.358$	$(10\bar{1})0.225$
	$\pm(100)0.280$	
μ, cm^{-1}	61.31	44.26
Transmission factors		
max	0.1728	0.6345
min	0.0562	0.2614
R	0.026	0.034
R_W	0.025	0.034
F(000)	344	808

refinement for $[Se(acac)]_2$ converged at $R = 0.026$ and $R_w = 0.025$, with $w = (\sigma^2(F) + 0.000008\ F^2)^{-1}$. The final difference map showed no peaks of heights > 0.40 e Å^{-3}. For $[PhSe]_2[acac]$ the refinement converged at $R = 0.034$ and $R_w = 0.034$, with $w = 1.4652(\sigma^2(F) + 0.00045\ F^2)^{-1}$. The final difference map showed no peaks with

Table 2

Final fractional atomic coordinates for $[Se(CH_3C(O)CC(O)CH_3)]_2$.

Atom	x	y	z
Se	0.08731(4)	0.08549(5)	−0.10009(2)
C(1)	0.3092(6)	0.1324(6)	0.1892(3)
C(2)	0.3320(5)	−0.0208(5)	0.1126(3)
C(3)	0.1637(5)	−0.0843(4)	0.0269(2)
C(4)	0.2029(5)	−0.2604(5)	−0.0247(3)
C(5)	0.2298(7)	−0.4017(5)	0.0665(4)
O(1)	0.4815(4)	−0.0990(3)	0.1154(2)
O(2)	0.2039(5)	−0.2835(3)	−0.1349(2)

Table 3

Final fractional atomic coordinates for $[PhSe]_2[CH_3C(O)CC(O)CH_3)]$

Atom	*x*	*y*	*z*
C(1A)	0.3089(7)	0.3385(7)	0.5290(4)
C(2A)	0.2091(5)	0.4219(6)	0.5745(3)
C(3A)	0.2465(4)	0.5430(5)	0.5877(3)
C(4A)	0.2768(5)	0.6435(6)	0.5102(3)
C(5A)	0.1885(6)	0.6697(7)	0.4342(3)
O(1A)	0.1037(4)	0.3942(5)	0.6001(3)
O(2A)	0.3676(4)	0.6986(4)	0.5114(2)
Se(1A)	0.41731(5)	0.48396(6)	0.66112(4)
C(6A)	0.3817(5)	0.3286(6)	0.7391(3)
C(7A)	0.4755(6)	0.2038(7)	0.7458(4)
C(8A)	0.4586(8)	0.0907(8)	0.8040(5)
C(9A)	0.3471(8)	0.1012(7)	0.8531(4)
C(10A)	0.2506(7)	0.2260(7)	0.8445(4)
C(11A)	0.2698(6)	0.3407(6)	0.7890(3)
Se(2A)	0.07302(5)	0.65004(7)	0.62675(3)
C(12A)	0.1469(5)	0.7894(6)	0.6446(3)
C(13A)	0.1302(6)	0.9099(6)	0.5829(4)
C(14A)	0.1699(7)	1.0153(6)	0.5979(4)
C(15A)	0.2263(6)	1.0023(6)	0.6731(4)
C(16A)	0.2462(7)	0.8822(7)	0.7323(4)
C(17A)	0.2056(6)	0.7744(6)	0.7198(3)
C(1B)	0.2830(6)	0.2572(6)	0.0582(4)
C(2B)	0.3521(5)	0.3385(5)	0.0929(3)
C(3B)	0.2564(5)	0.4707(5)	0.1053(3)
C(4B)	0.1658(5)	0.5677(5)	0.0302(3)
C(5B)	0.2320(6)	0.5876(7)	−0.0503(3)
O(1B)	0.4771(4)	0.3018(4)	0.1130(2)
O(2B)	0.0454(4)	0.6294(4)	0.0360(2)
Se(1B)	0.11978(5)	0.42820(6)	0.18763(3)
C(6B)	0.2403(5)	0.2737(5)	0.2676(3)
C(7B)	0.2059(6)	0.1519(6)	0.2857(3)
C(8B)	0.2807(7)	0.0416(6)	0.3490(4)
C(9B)	0.3897(6)	0.0535(6)	0.3915(3)
C(10B)	0.4260(6)	0.1736(6)	0.3730(3)
C(11B)	0.3491(6)	0.2833(6)	0.3117(3)
Se(2B)	0.38842(6)	0.56579(6)	0.13338(3)
C(12B)	0.2524(5)	0.7323(6)	0.1345(3)
C(13B)	0.2366(7)	0.8460(6)	0.0691(4)
C(14B)	0.1421(9)	0.9697(7)	0.0697(5)
C(15B)	0.0666(8)	0.9762(8)	0.1359(5)
C(16B)	0.0801(8)	0.8655(8)	0.2015(5)
C(17B)	0.1729(7)	0.7422(7)	0.2009(4)

heights > 0.49 e Å^{-3}. Calculations were carried out by use of the programs SHELX-76 [4], ORTEP [5], DISTAN [6] and MEAN PLANE [7] on a VAX 11/780 computer at the University Computer Services, University of Melbourne. Scattering curves for atomic H, C, and O were those collected by Sheldrick [4], while that of Se was taken from ref. 8, the value being corrected for the real and imaginary dispersion terms [9]. Final fractional atomic coordinates are given in Tables 2 and 3. Tables of structure factors and thermal parameters are available from the authors.

Table 4

Selected bond lengths (Å) and angles (deg) for $[Se(CH_3C(O)CC(O)CH_3]_2$.

Se–C(3)	1.965(3)	C(2)–O(1)	1.213(5)
Se–C(3^{I}) ^{a}	1.981(3)	C(2)–C(3)	1.529(5)
Se...Se^{I}	2.9007(4)	C(3)–C(4)	1.529(5)
C(3)...C(3^{I})	2.675(5)	C(4)–O(2)	1.209(4)
C(1)–C(2)	1.481(6)	C(4)–C(5)	1.429(6)
Se...O(2)	3.051(3)	Se...O(1^{II})	3.036(3)
Se–C(3)–Se^{I}	94.6(1)	C(1)–C(2)–O(1)	121.9(3)
C(3)–Se–C(3^{I})	85.4(1)	C(3)–C(2)–O(1)	118.2(3)
Se–C(3)–C(2)	111.1(2)	C(2)–C(3)–C(4)	111.6(3)
Se–C(3)–C(4)	114.1(2)	C(3)–C(4)–C(5)	116.9(3)
Se^{I}–C(3)–C(2)	115.1(2)	C(3)–C(4)–O(2)	120.8(3)
Se^{I}–C(3)–C(4)	109.3(2)	C(5)–C(4)–O(2)	122.2(4)
C(1)–C(2)–C(3)	119.8(3)	C(3)–Se–O(1^{II})	80.9(1)
C(3)–Se–O(2)	51.43(9)	C(3^{I})–Se–O(1^{II})	159.51(8)
C(3^{I})–Se–O(2)	107.4(1)	O(1^{II})–Se–O(2)	75.56(8)

^{a} I: $-x, -y, -z$; II: $1-x, -y, -z$.

Description of the structure of [Se(acac)]$_2$

Bond lengths and angles are given in Table 4. The structure of $[Se(acac)]_2$ comprises centrosymmetric units formed by two acac ligands bridging a pair of selenium atoms via the methine carbon atoms, as shown in Fig. 1. The lengths of the two Se–C bonds are similar (1.965(3), 1.981(3) Å). The $[Se_2C_2]$ ring is approximately square planar, the Se–C–Se angle being 84.4(1)°, while the two selenium atoms are separated by 2.9007(4) Å. The Se–Se separation is somewhat longer than the sum of their covalent radii, but much shorter than the sum of the Van der Waals radii [10]. This situation appears to arise not because of any identifiable bonding interaction between the two selenium atoms but rather because of the steric restraints imposed by the two bridging methine carbon atoms.

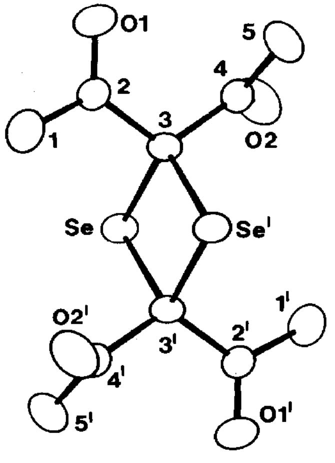
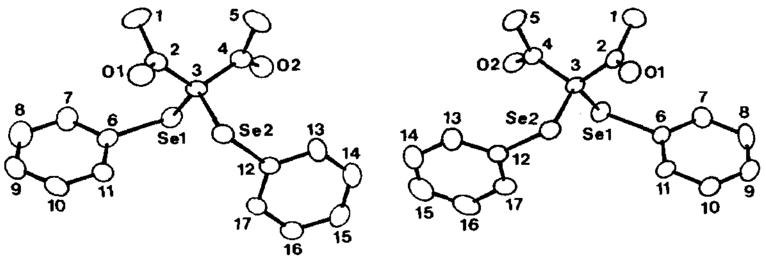


Fig. 1. ORTEP diagram of $[Se(acac)]_2$ showing the numbering scheme employed. Atoms not otherwise indicated are carbon atoms. Primed atoms are related to those given in Table 1 by $-x, -y, -z$.



(A) (B)

Fig. 2. ORTEP diagram of the two molecules, A and B, of $[PhSe]_2[acac]$ showing the approximate mirror relationship. Atoms not otherwise indicated are carbon atoms.

Table 5

Selected bond lengths (Å) and angles (deg) for $[Ph_2Se]_2[CH_3C(O)CC(O)CH_3]$

	Moleule A	Molecule B
Se(1)-C(6)	1.924(6)	1.927(5)
Se(2)-C(12)	1.922(6)	1.910(6)
Se(1)-C(3)	1.961(5)	1.970(5)
Se(2)-C(3)	1.989(5)	1.991(5)
Se(1)...Se(2)	3.3265(8)	3.3456(8)
Se(1)...O(1)	3.714(4)	3.727(4)
Se(1)...O(2)	2.861(4)	2.822(4)
Se(2)...O(1)	2.830(5)	2.831(4)
Se(2)...O(2)	3.536(4)	3.591(4)
C(1)-C(2)	1.496(9)	1.484(8)
C(2)-O(1)	1.192(7)	1.204(7)
C(2)-C(3)	1.513(8)	1.532(8)
C(3)-C(4)	1.535(7)	1.519(7)
C(4)-O(2)	1.197(7)	1.199(7)
C(4)-C(5)	1.496(7)	1.498(7)
Se(1)-C(3)-Se(2)	114.7(2)	115.3(2)
C(6)-Se(1)-C(3)	99.9(2)	101.0(2)
C(12)-Se(2)-C(3)	98.9(2)	98.9(2)
Se(1)-C(3)-C(2)	110.9(4)	109.6(3)
Se(1)-C(3)-C(4)	106.0(3)	105.2(3)
Se(2)-C(3)-C(2)	106.1(3)	105.5(3)
Se(2)-C(3)-C(4)	104.2(4)	106.8(3)
C(1)-C(2)-C(3)	117.8(5)	117.2(5)
C(1)-C(2)-O(1)	121.6(6)	122.3(5)
C(3)-C(2)-O(1)	120.6(5)	120.5(5)
C(2)-C(3)-O(4)	115.0(4)	114.8(4)
C(3)-C(4)-C(5)	117.5(5)	118.4(5)
C(3)-C(4)-O(2)	120.6(4)	120.4(4)
C(5)-C(4)-O(2)	121.9(5)	121.1(5)
C(3)-Se(1)-O(2)	55.4(2)	55.8(2)
C(6)-Se(1)-O(2)	154.8(2)	156.3(2)
C(3)-Se(2)-O(1)	55.2(2)	56.0(2)
C(12)-Se(2)-O(1)	152.9(2)	154.8(2)

The selenium atoms also coordinate to two oxygen atoms, an intermolecular interaction with O(2) (3.051(3) Å), and an intramolecular interaction with O(1^{II}) (3.036(3) Å) (where ^{II} refers to the atom related by the symmetry operation $1-x$, $-y$, $-z$ to the coordinates in Table 2), both are significantly less than the sum of the Van der Waals radii of 3.42 Å [10]. The environment about the Se atom is a distorted octahedron involving two stereochemically active lone electron pairs. The intramolecular Se–O(1^{II}) interaction results in a linear polymer, which lies along the *c*-axis.

Description of the structure of [PhSe]$_2$[acac]

The atomic labelling scheme is shown in Fig. 2, and the bond lengths and angles appear in Table 5. There are two independent molecules within the unit cell that appear to differ only in the configuration of the phenyl and acac ligands. The difference is such that when viewed down the Se–Se direction of each molecule, there is a pseudo mirror plane, although no symmetry element other than $\bar{1}$ is present in the unit cell. Each Se atom is bonded to two carbons and one (intermolecular) oxygen at approximately 2.82 Å (Table 5). A second oxygen, from an adjacent molecule, is at approximately 3.5 Å from the Se atom. This latter Se–O separation is expected on the basis of the Van der Waals radii, and there is no actual bridging. The Se–Se distance is about 3.4 Å and the Se–C–Se angle is slightly greater than the terahedral angle. Apparently the steric restraints are significantly smaller than those in [Se(acac)]$_2$, and the selenium atoms are able to move further apart, although their separation is still appreciably less than the sum of their Van der Waals radii [10]. The environment at each Se atom can be considered to be a distorted trigonal bipyramid containing three atoms and two lone electron pairs, with the lone pairs in the equatorial plane.

Acknowledgement

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