

135. *The Constitution of the Acetylacetonate Derivatives of Sulphur, Selenium, and Tellurium.*

By (Miss) D. H. DEWAR, J. E. FERGUSSON, P. R. HENTSCHEL,
C. J. WILKINS, and P. P. WILLIAMS.

Evidence from nuclear magnetic resonance and optical spectra indicates structures (I—VIII) for acetylacetonate derivatives of sulphur, selenium, and tellurium.

SULPHUR, selenium, and tellurium form several types of acetylacetonate derivatives. The chemical evidence¹ points to more than one mode of attachment of the ligand, probably with bonding to carbon rather than to oxygen in most cases. We now report spectroscopic information on the constitution of representative compounds.

Sulphur bisacetylacetonate^{1a*} and disulphur bisacetylacetonate^{1b*} obtained from the respective reactions of sulphur dichloride and sulphur monochloride with acetylacetonate give almost identical nuclear magnetic resonance spectra (Table 1), with the

TABLE I.
Proton resonance chemical shifts.

		Chemical shift (c./sec.)	Relative intensity
(I)	S(C ₅ H ₇ O ₂) ₂	141, 1009	6 : 1
(II)	S ₂ (C ₅ H ₇ O ₂) ₂	142, 1026	6 : 1
(III)	Se ₂ (C ₅ H ₇ O ₂) ₂	153	6*
(IV)	Se ₂ (C ₅ H ₇ O ₂) ₂	146, 1021	6 : 1
(V)	Se(C ₅ H ₇ O ₂) ₂	143, 147, 253, 1047	6 : 6 : 1 : 1
(VI)	Te(C ₅ H ₇ O ₂) ₂	207, 234	1 : 2
(IX)	Te(C ₅ H ₆ ClO ₂) ₂ Cl ₂	140, 292, 879	3 : 2 : 1

* Absolute intensity.

expected 6 : 1 intensity ratios for the two peaks. The weaker peaks, for which the chemical shifts are 1009 and 1026 c./sec., must be ascribed to hydrogen-bonding protons² in structures (I) and (II) rather than to uniquely situated protons remaining on carbon as in metal acetylacetonates. Infrared spectra of the two compounds are correspondingly similar. The C—H out-of-plane bending absorption at 770—780 cm.⁻¹ characteristic of

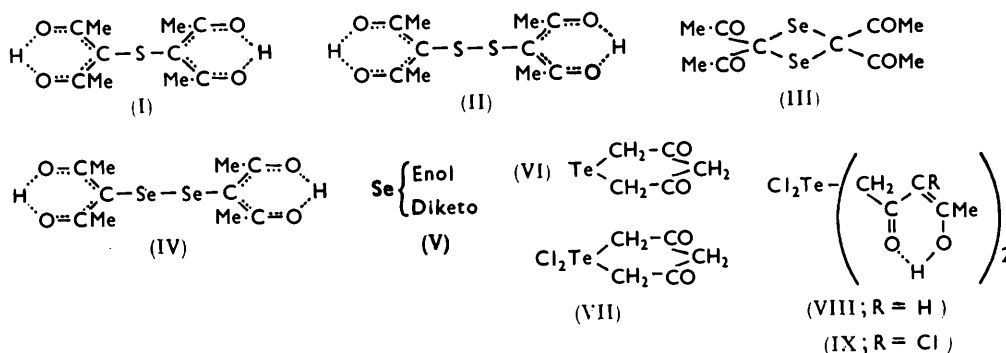
• Systematic names for these and the other compounds, based on the structures advocated in this Paper, are given in the Experimental section.

¹ (a) Magnani and Angeli, *Gazzetta*, 1894, **24**, I, 342; (b) Vaillant, *Compt. rend.*, 1894, **119**, 647; (c) Morgan and Drew, *J.*, 1920, **117**, 1456; (d) Morgan, Drew, and Barker, *J.*, 1922, **121**, 2432; (e) Morgan and Drew, *ibid.*, p. 922.

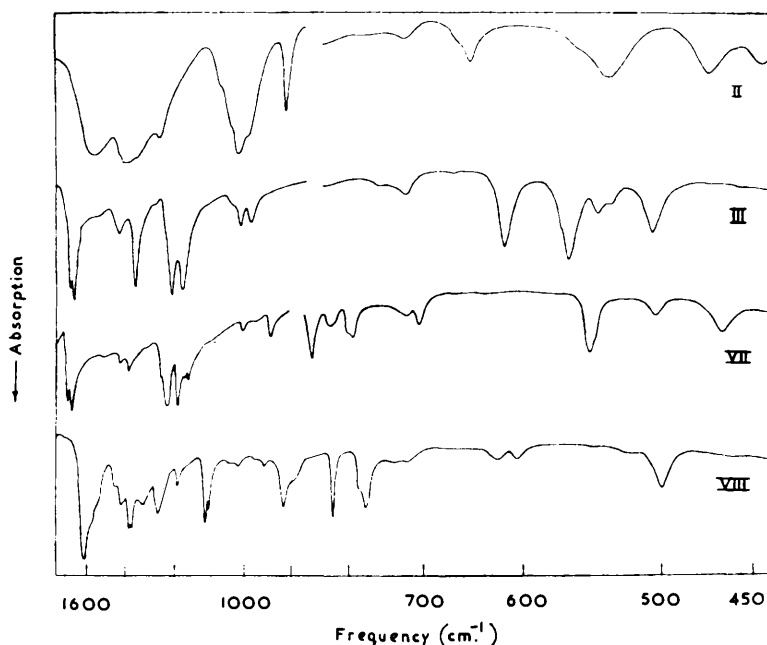
² Jarrett, Sadler, and Shoolery, *J. Chem. Phys.*, 1953, **21**, 2092.

metal acetylacetonates³ is absent, and displacement of the C=O stretching frequency from 1725 cm.⁻¹ (in acetylacetonate) to 1560 cm.⁻¹ is evidence of chelation.^{3,4} The disulphur compound gives bands at 472 and 446 cm.⁻¹ which may be associated with the S-S linkage.

Three acetylacetonates of selenium are known. The chief product (III) from the reaction between selenium tetrachloride and acetylacetonate is of composition Se₂(C₅H₆O₂)₂.^{1c}



It is reduced quantitatively by hydriodic acid to compound (IV), with uptake of one proton per ligand.^{1d} Reaction of compound (III) with acetylacetonate is stated to yield a material (V), Se(C₅H₇O₂)₂,^{1d} which is obtained also by reaction of selenium tetrachloride



Infrared spectra of compounds designated.

with copper acetylacetonate. In confirmation of the ratio H : Se = 6 : 1, the compound (III) gives a single proton resonance of absolute intensity 6. All the protons are therefore contained within symmetrically placed methyl groups and only the formulation as tetraacetyldiselenacyclobutane appears to fulfil this requirement. The compound has a relatively simple infrared spectrum (Figure) with a C=O band at 1706 cm.⁻¹. Absorptions

³ Nakamoto, McCarthy, and Martell, *J. Amer. Chem. Soc.*, 1961, **83**, 1066, 1272.

⁴ West, *J. Amer. Chem. Soc.*, 1958, **80**, 3246.

due to ring vibrations shown by metal chelate acetylacetonates in the ranges 1260—1300 and 660—685 cm^{-1} are absent.³ The reduction product (IV) is isomorphous with (II). The nuclear magnetic resonance (n.m.r.) spectra of these two compounds confirm the identity of their structures in solution.

The n.m.r. spectrum of compound (V), which has a pair of almost equally strong methyl resonances, suggests two dissimilar but symmetrical ligands, one of which is closed by the single proton giving the peak at 1047 c./sec. A group of infrared absorptions reproducing the spectrum of compound (V) arises from this ligand. The remaining infrared peaks at 1690, 1352, 1155, and 950 cm^{-1} correspond with absorptions shown by compound (III), by acetylacetonate and (except 1155 cm^{-1}) by acetone. Since chelation through oxygen is excluded by the presence of the C=O absorption (1690 cm^{-1}),^{3,4} the evidence points to the diketo-form of the ligand with which the peak at 253 c./sec. is in accord. It seems probable that the one ligand is retained in the diketo-form to relieve steric congestion. Examination of a molecular model showed that, with a selenium bond angle of about 96° or lower, the interference is considerable unless one of the ligands reverts from the enol to the diketo-form. The existence of both ligands of compound (I) in the enol form suggests that the sulphur bond angle is greater than that of selenium.

Of the tellurium compounds, one material ($\text{TeC}_5\text{H}_8\text{O}_2$)^{1c} has an n.m.r. spectrum with two peaks of relative intensity 2 : 1, corresponding to the telluracyclohexane-3,5-dione structure (VI). The infrared spectrum contains a free carbonyl absorption. The chlorides, $\text{Te}(\text{C}_5\text{H}_8\text{O}_2)\text{Cl}_2$ ^{1c} (VII) and $\text{Te}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$ ^{1c} (VIII), are too insoluble for the recording of n.m.r. spectra. But the optical spectra of compounds (VI) and (VII) leave little doubt as to the identity of the ring systems in the two compounds. The ultraviolet absorption maxima lie at the same wavelengths (Table 2), and, apart from differences in the region 1180—1130 cm^{-1} , the infrared spectra are similar. A strong absorption shown by compound (VII) at 400 cm^{-1} , and by compound (VIII) (at 391 cm^{-1}) [but not by (VI)], may be assigned tentatively to the Te-Cl stretching vibration.

Infrared spectra point to structural similarity of compound (VIII) and the chloroform-soluble tellurium bis-3-chloroacetylacetonate dichloride^{1c} (IX) whose n.m.r. spectrum indicates linkage of hydrogen-bond chelate ligands each through one terminal carbon. The infrared spectra of these compounds lack the free carbonyl absorptions given by (the keto-forms of) the parent diones.⁵ Compound (VIII) shows the distinctive out-of-plane bending frequency (774 cm^{-1}) associated with the chelate ring.³ Both compounds give strong absorptions, compound (VIII) at 1104, 1094, and 825 cm^{-1} , and (IX) at 1120 and 816 cm^{-1} , which are shown neither by metal acetylacetonates nor by the tellurium compounds (VI) and (VII). Otherwise the spectra of compounds (VIII) and (IX) show general similarities to those of the respective 1,3-diones.

The structures found for compounds (I), (II), (IV), (VIII), and (IX) differ from earlier proposals only in the hydrogen-bond closure of the ligand ring. Structure (III) has merit over the original suggestion in not requiring multiple bonding of bivalent selenium. The same four-membered ring may occur also in the dimeric selenoketones.⁶ The tellurium acetylacetonates obtained directly from the condensation differ from the selenium compounds in containing tellurium, in oxidation state 4, linked to terminal carbon atoms. The existence of compounds (VI) and (VII) purely in the diketo-form in solution but of (VIII) and (IX) in the enol form affords evidence that enolisation occurs only under the stimulus of hydrogen-bond chelation.

EXPERIMENTAL

Infrared spectra of mulls were recorded over the range 5000—300 cm^{-1} by using a Perkin-Elmer 221 spectrophotometer. Ultraviolet spectra (Table 2) were obtained in chloroform

⁵ (a) Bratoz, Hadzi, and Rossmly, *Trans. Faraday Soc.*, 1956, **52**, 464; (b) Belford, Martell, and Calvin, *J. Inorg. Nuclear Chem.*, 1956, **2**, 11.

⁶ Lyons and Bradt, *Ber.*, 1927, **60**, 824.

solution. Proton resonance spectra were run in deuteriochloroform on a Varian HR60 spectrometer (6×10^7 c./sec.) with tetramethylsilane as internal standard.

TABLE 2.

Compound	$\lambda_{\max.}$ (m μ)	ϵ	Compound	$\lambda_{\max.}$ (m μ)	ϵ
(I)	288	13,550	(VI)	243, 306	94,800, 51,500
(II)	291, 336	86,800, 55,000	(VII)	243, 308	63,500, 14,200
(III)	286	16,450	(VIII)	290	12,300
(IV)	287	28,600	(IX)	315	23,000
(V)	281	8430			

Preparation and Characterisation of the Acetylacetonate Derivatives.—The compounds were prepared essentially by methods given in the literature.¹ 3,3'-Thiodi-(4-hydroxypent-3-en-2-one) (I) [Found: C, 52.15; H, 6.1%; *M* (cryoscopic in C_6H_6), 236. Calc. for $C_{10}H_{14}O_4S$: C, 52.6; H, 6.1%; *M*, 230] formed acicular crystals that collapsed at 68° and melted at 73°. In the purification of 3,3'-dithiodi-(4-hydroxypent-3-en-2-one) (II), m. p. 90–92°, ether was the most efficient solvent for recrystallisation [Found: C, 45.6; H, 5.4%; *M* (isopiestic in $CHCl_3$), 270. Calc. for $C_{10}H_{14}O_4S_2$: C, 45.8; H, 5.3%; *M*, 262].

2,2,4,4-Tetra-acetyl-1,3-diselenacyclobutane (III) was recrystallised from benzene in subdued light [Found: C, 34.1; H, 3.3%; *M* (isopiestic in C_6H_6), 330. Calc. for $C_{10}H_{12}O_4Se_2$: C, 33.9; H, 3.4%; *M*, 354]. Its reduction product, 3,3'-diselenodi-(4-hydroxypent-3-en-2-one) (IV), had m. p. 78° [Found: C, 33.9; H, 4.3%; *M* (cryoscopic in C_6H_6), 347. Calc. for $C_{10}H_{14}O_4Se_2$: C, 33.7; H, 4.0%; *M*, 356].

3-(1-Acetyl-2-hydroxypropenylseleno)pentane-2,4-dione (V) was obtained (0.6 g.) by shaking selenium tetrachloride (4.4 g.) and anhydrous copper acetylacetonate (21.2 g.) suspended in cold, dry, alcohol-free chloroform (180 ml.) for 2 hr. The chloroform layer was then shaken with the minimum quantity of dilute sulphuric acid to decompose the copper complex, and the solvent removed under a vacuum. The product, m. p. 45° (decomp.), was recrystallised from light petroleum (b. p. 40–60°) [Found: C, 43.5; H, 5.4%; *M* (cryoscopic in C_6H_6), 280. Calc. for $C_{10}H_{14}O_4Se$: C, 43.3; H, 5.1%; *M*, 277]. The crystals obtained from chloroform (needles and wart-like encrustations) differ from those from light petroleum.^{1d} Yet their spectra were identical and almost the same as that given by the stable solution in chloroform. Attempts to obtain a preparation having a higher proportion of the enol form of the ligand by recrystallisation from acetone and by treatment with di- or tri-ethylamine gave only decomposition products.

1,1-Dichlorotelluracyclohexane-3,5-dione (VII) formed silver-white crystals, darkening at 146° and melting with decomposition at 162° [Found: C, 19.7; H, 2.2; Cl, 24.5; *M* (isopiestic in $CHCl_3$), 298. Calc. for $C_6H_8Cl_2O_2Te$: C, 20.2; H, 2.0; Cl, 23.95%; *M*, 296.7]. Its yellow reduction product, telluracyclohexane-3,5-dione (VI), was recrystallised from water and dried under a vacuum [Found: C, 26.6; H, 2.65%; *M* (isopiestic in C_6H_6), 276. Calc. for $C_6H_8O_2Te$: C, 26.6; H, 2.7; *M*, 226]. 1,1'-(Dichlorotelluro)di-(4-hydroxypent-3-en-2-one) (VIII) [Found: C, 30.5; H, 3.2; Cl, 17.6%; *M* (isopiestic in acetone), 397. Calc. for $C_{10}H_{14}Cl_2O_4Te$: C, 30.3; H, 3.6; Cl, 17.85%; *M*, 396.6] was obtained as a by-product from the preparation of (VII) only when dry alcohol-free chloroform was used as solvent. The respective molar conductivities of (VII) and (VIII) in dimethylformamide at 25° are 4.8 and 3.1 ohm⁻¹ cm.² (as compared with 60–80 for a fully dissociated 1 : 1 electrolyte).

1,1'-(Dichlorotelluro)di-(3-chloro-4-hydroxypent-3-en-2-one) (IX) was prepared as described^{1e} [Found: C, 26.1; H, 2.8%; *M* (cryoscopic in $CHBr_3$), 460. Calc. for $C_{10}H_{12}Cl_4O_4Te$: C, 25.8; H, 2.6%; *M*, 465].

Tellurium tetrachloride and tetrabromide failed to react with trifluoroacetylacetonate alone under reflux or in chloroform or toluene at the b. p. or 140°. Nor did tellurium tetrachloride react with hexafluoroacetylacetonate.

Isomorphism of Compounds (II) and (IV).—This is shown by the *d* values from X-ray powder photographs: (IV) 6.06s, 5.67m, 5.10m, 4.70m, 3.62m, 3.42m, 3.21ms, 3.13m, and 2.60m. (II) 6.04s, 5.58w, 5.02w, 4.61m, 3.56ms, 3.36m, 3.28m, 3.17s, and 3.10m.

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UNIVERSITY OF CANTERBURY, CHRISTCHURCH, NEW ZEALAND.
DOMINION LABORATORY, PETONE, NEW ZEALAND.

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