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Mendeleev Commun., 2022, **32**, 12–15

Mendeleev Communications

Hypercoordinate germanium complexes with phenanthrene-9,10-diolate ligands: synthesis, structure, and electronic properties

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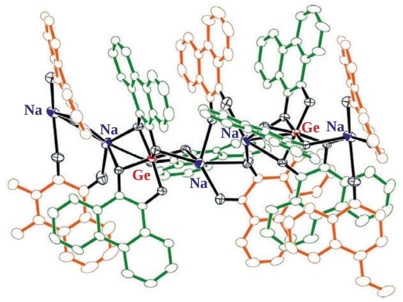
DOI: 10.1016/j.mencom.2022.01.003

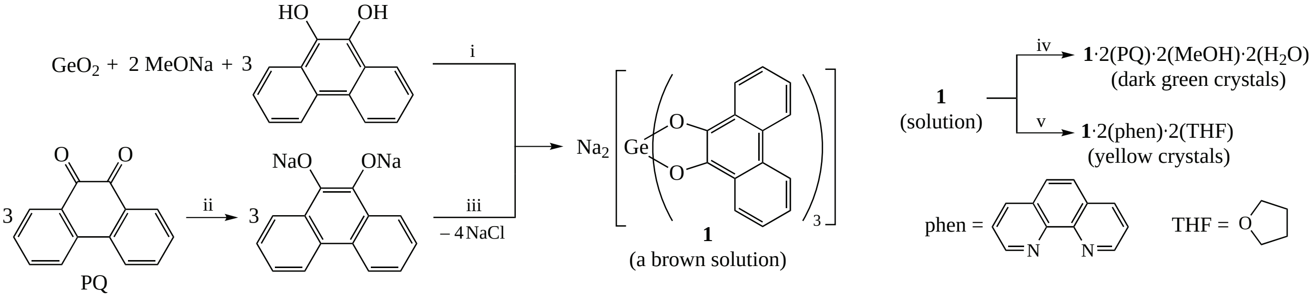
The synthesis, molecular structure, and electronic properties of sodium tris(phenanthrene-9,10-diolato)germanate(IV) are described. The germanate complex is readily oxidized in air to produce 9,10-phenanthrenequinone, and the resulting quinones and the ligands reveal intermolecular π-stacking interaction in the polymeric association in the solid state. Addition of phenanthroline to the germanate complex leads to a monomeric structure.



Keywords: emission spectrum, germanate complexes, phenanthrene-9,10-diolate, hypercoordinate, π-stacking, UV-VIS spectrum, X-ray diffraction analysis.

Unlike the carbon system, hypercoordinated heavier group-14 element compounds, such as silicates or germanates, are isolable and have been studied for a long time.[1–5] Since Corriu *et al*. reported six-coordinate silicates[6] and germanates[7,8] having catecholate ligands, a number of interesting works have been published. Greb *et al*. reported octahedral triplet biradical silicate species using perchlorinated 1,2-catecholate ligands.[9,10] They also described a super Lewis acid of germanium compounds bearing perchlorocatecholate ligand.[11] Baines *et al*. first reported six-coordinate germanate species having a 3,5-di-*tert*-butylcatecholate ligand and proposed a new halogen-free synthesis of organogermanium compounds *via* these germanate complexes,[12] and this was quickly followed by Syroeshkin *et al*.[13,14] In fused aromatic compounds, the HOMO–LUMO gap decreases as the number of rings increase due to the extension of π-conjugation.[15] Phenanthrene molecule is formed from three benzene rings and is a structural isomer of anthracene. We started our research with an interest in the structure and optical properties of octahedral hypercoordinated germanium complexes bearing phenanthrene-9,10-diolate ligands.

When germanium oxide and three equivalents of phenanthrene-9,10-diol were added to a methanol solution containing two molar equivalents of sodium methoxide and heated under inert atmosphere, a clear brown solution containing sodium tris(phenanthrene-9,10-diolato)germanate(IV) **1** was obtained (Scheme 1). Removal of the solvent from the solution under reduced pressure gave a greenish brown solid of product **1** (85% yield) which was characterized by ^{1}H and ^{13}C NMR spectroscopy. When the clear brown solution of **1** was exposed to air, the colour instantly changed to green and dark green crystals precipitated. These crystals were fully characterized by ^{1}H and ^{13}C NMR spectroscopy in THF-d_8 and by elemental analysis. According to the elemental analysis, the composition could be represented by **1**·2(PQ)·2(MeOH)·2(H$_2$O), where PQ denotes 9,10-phenanthrenequinone. The characteristic signal of the carbonyl carbon of PQ was observed at 179.6 ppm in ^{13}C NMR spectrum. Since PQ was not used in the synthesis, PQ could result from the oxidation of **1**. In order to investigate the detailed molecular structure, we prepared a single crystal by recrystallization from MeOH/DMSO (20 : 1) mixed solvent and performed X-ray crystallographic analysis.



Scheme 1 *Reagents and conditions*: i, MeONa (2 equiv.), MeOH, reflux; ii, Na metal (6 equiv.), THF; iii, GeCl$_4$, THF; iv, exposed to the air, MeOH; v, phenanthroline (2 equiv.), THF.

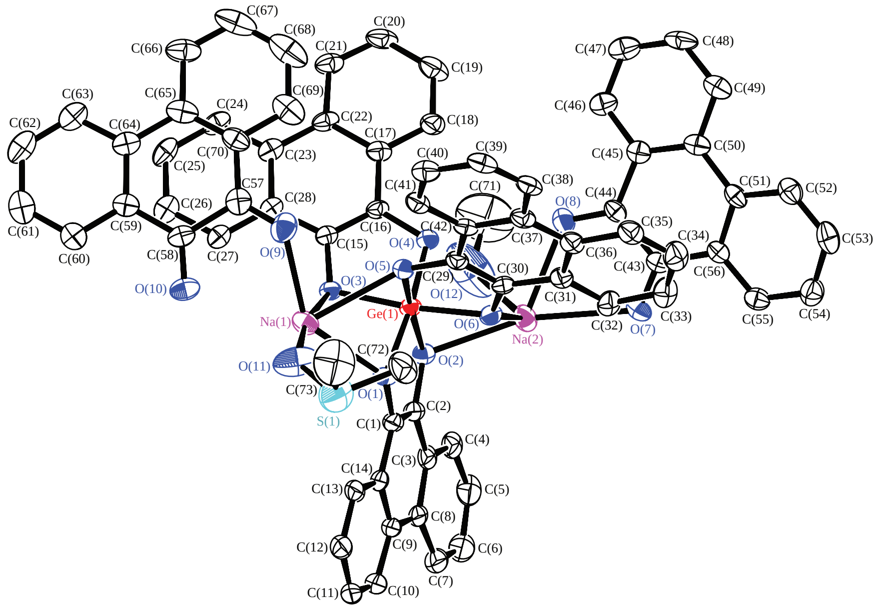


Figure 1 Molecular structure of **1**·2(PQ)·(DMSO)·3(MeOH). Hydrogen atoms and clathrate two methanol molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge(1)–O(1) 1.887(3), Ge(1)–O(2) 1.914(3), Ge(1)–O(3) 1.907(3), Ge(1)–O(4) 1.881(3), Ge(1)–O(5) 1.885(3), Ge(1)–O(6) 1.899(3); O(1)–Ge(1)–O(2) 86.62(13), O(1)–Ge(1)–O(3) 87.28(13), O(1)–Ge(1)–O(4) 172.67(14), O(1)–Ge(1)–O(5) 88.19(13), O(1)–Ge(1)–O(6) 97.36(13), O(2)–Ge(1)–O(5) 171.83(13), O(3)–Ge(1)–O(6) 173.66(13).

The molecular structure of the dark green single crystal contained two molecules of PQ, one molecule of DMSO and three molecules of methanol, **1**·2(PQ)·(DMSO)·3(MeOH), based on **1** as shown in Figure 1.[†] Structural differences between phenanthrene-9,10-diolate ligands (PLs) and clathrate PQs are substantial. The C–O bond lengths in PLs are within the range of 1.348–1.371 Å, which are apparently longer than those in PQs (the C=O bond lengths of 1.215–1.225 Å). Three PLs are coordinated to germanium centre to form octahedral configuration. The Ge–O bond lengths are within the range from 1.881 Å [Ge(1)–O(4)] to 1.914 Å [Ge(1)–O(2)]. The Ge–O bonds in **1**·2(PQ)·(DMSO)·3(MeOH) are longer than those found in octahedral bis(3,5-di-*tert*-butylcatecholato)germanium tetramethylethylenediamine adduct (1.8457–1.856 Å)[12] due to the weaker donor nature of PL. The bond angles O(1)–Ge(1)–O(4), O(2)–Ge(1)–O(5), and O(3)–Ge(1)–O(6) are 172.62, 171.83, and 173.66°, respectively, which deviate from linear form, suggesting that the octahedral configuration is slightly distorted. The Na(1) atom is coordinated by three oxygen atoms in phenanthrene-9.10-diolate ligands [O(1), O(3), and O(5)], two oxygen atoms in clathrate PQ molecules [O(9) and O(11)], and one oxygen atom in DMSO molecule [O(11)]. On the other hand, the Na(2) atom is bound to total six oxygen atoms in PLs [O(2) and O(6)], PQ molecules [O(7), O(8), and O(10)], and methanol [O(12)]. One of the PQ molecules and DMSO molecule play a role of bridges between two sodium atoms to form polymer-like association structure in the crystal as shown in Figure 2. Interestingly, four phenanthrene rings (two of four are PLs and the rest are clathrate PQs) are arranged partially in parallel, the nearest interatomic distance is 3.112 Å [C(13)–C(43*)]. The distance between the two phenanthrene planes is about 3.2 Å, which is comparable to the interlayer distance of graphite (3.35 Å).[16] This stack seems to reflect a π-stacking interaction between PL and PQ, as it was also observed in tris(9,10-phenanthrenesemiquinone)iron(III)[17] and bis(9,10-phenanthrenesemiquinone)(bipyridine)nickel(II)[18] complexes, in which phenanthrene rings are stacked with the interligand distances of 3.3–3.5 Å. Furthermore, this structural feature of π-stacking in **1**·2(PQ)·(DMSO)·3(MeOH) might be closely related to the dark green colour in the solid state.

When the dark green solid of **1**·2(PQ)·2MeOH·2H_2O was dissolved in THF, the colour of the solution became yellow. In the UV-VIS spectrum of the dilute solution [Figure 3(*a*)], the absorption maxima were observed at 306 nm ($\varepsilon = 2.07\times10^4$ dm^3 mol^{-1} cm^{-1}), 337 nm ($\varepsilon = 3.54\times10^4$ dm^3 mol^{-1} cm^{-1}), 349 nm ($\varepsilon = 3.31\times10^4$ dm^3 mol^{-1} cm^{-1}), and 410 nm ($\varepsilon = 9.1\times10^3$ dm^3 mol^{-1} cm^{-1}). The absorption bands at 306 and 410 nm are due to π–π* transition of PQ, while the 337 and 349 nm absorption bands are derived from germanate complex **1**. The UV-VIS spectrum was measured in a concentrated solution of **1**, however no absorption was observed in the long wavelength region above 470 nm. It suggests that germanate complex **1** and PQ molecule no longer form an associate but are thought to form solvent-separated independent molecules or complexes. A fluorescence of **1** was observed at 471 nm (λ_{ex} = 337 nm) as shown in Figure 3(*b*). Since no fluorescence is observed with PQ alone at room temperature,[19] the fluorescence should be derived from germanate complex **1**. The dark green solid was dispersed in KBr powder to make a molded pellet, and the UV-VIS spectrum of the pellet was measured [see inset of Figure 3(*a*)]. Very broad absorption was observed at λ_{max} = 438 nm, and the weak absorption band was also detected above 600 nm, probably due to a CT band between π-stacked PL and PQ in the solid state.

The reason why PQs are produced by oxidation of **1** in air is probably the occurrence of an equilibrium ligand exchange in

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[†] *Crystal data for* **1**·2(PQ)·(DMSO)·3(MeOH). $C_{75}H_{58}Ge_2Na_2O_{14}S$, M_w = 1333.90, monoclinic, $P2_1/n$ (No. 14), a = 16.159(5), b = 19.029(6) and c = 19.759(5) Å, β = 94.804(8)°, V = 5983(3) Å^3, Z = 4, d_{calc} = 1.481 g cm^{-3}, μ(Mo$K\alpha$) = 6.345 cm^{-1}, number of unique reflections is 13581, number of variables is 835, R [$I > 2\sigma(I)$] = 0.0654, wR_2 (all data) = 0.1633, GOF = 0.835.

Crystal data for **1**·2(phen)·2(THF). $C_{74}H_{56}GeN_4Na_2O_8$, M_w = 1247.85, monoclinic, $P2_1/c$ (No. 14), a = 23.3472(16), b = 12.9426(9) and c = 23.3144(18) Å, β = 124.728(3)°, V = 5790.0(7) Å^3, Z = 4, d_{calc} = 1.431 g cm^{-3}, μ(Mo$K\alpha$) = 6.345 cm^{-1}, number of unique reflections is 13101, number of variables is 802, R [$I > 2\sigma(I)$] = 0.0732, wR_2 (all data) = 0.1053, GOF = 0.956.

CCDC 2105597 and 2105601 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

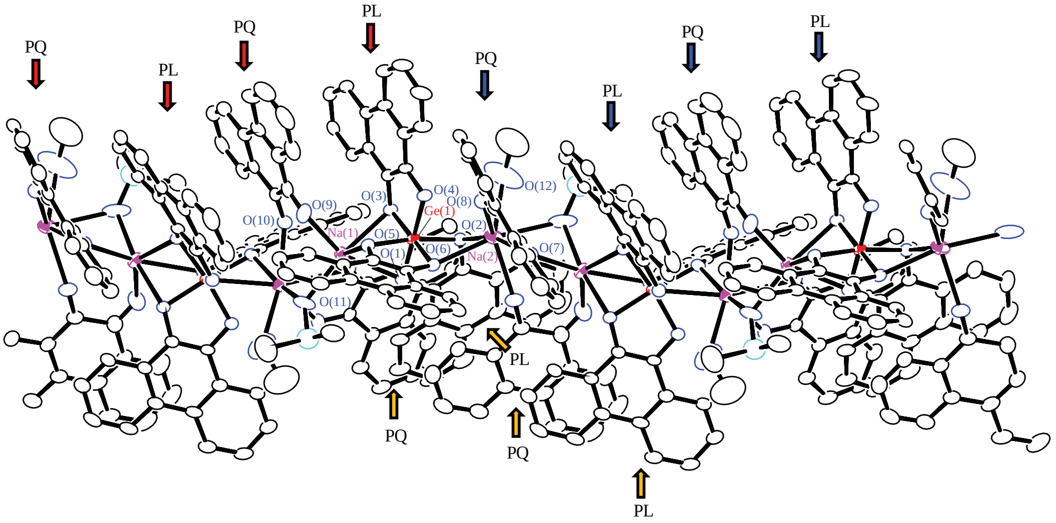

Figure 2 Polymeric association of **1**·2(PQ)·(DMSO)·3(MeOH). Hydrogen atoms and clathrate two methanol molecules are omitted for clarity.

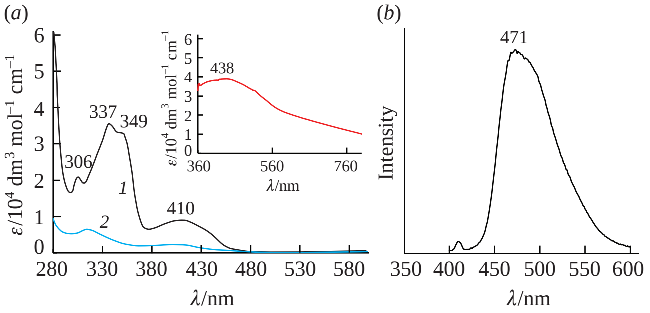

Figure 3 (*a*) UV-VIS spectra of (*1*) **1** (black) and (*2*) PQ (blue) in THF. The inset is UV-VIS spectrum of **1** in a KBr pellet. (*b*) Fluorescence spectrum of **1** in THF at room temperature. Excitation wavelength is 337 nm.

protic methanol to afford phenanthrene-9,10-diol which readily undergoes oxidation in air to produce PQ. To obtain complex **1** without any PQs, we attempted to perform the synthesis in aprotic THF (see Scheme 1). Sodium phenanthrene-9,10-diolate generated by the reaction of PQ with sodium metal in THF was reacted with tetrachlorogermane to give sodium germanate **1** as greenish brown solid. The similar fluorescence [see Figure 3(*b*)] of this substance was also observed (see Online Supplementary Materials, Figure S5). However, this solid reacted with oxygen immediately when exposed to air and turned into a dark green solid, suggesting that the resulting solid could contain PQ molecules. Meanwhile, addition of two equivalents of phenanthroline to **1** in THF yielded yellow air-stable precipitate. As a yellow single crystal was obtained by the recrystallization from THF, X-ray crystallographic analysis was performed (Figure 4).† The crystal contains two phenanthroline molecules and two THF molecules based on germanate complex **1**. The composition of yellow crystal is **1**·2(phen)·2(THF). In contrast to the phenanthroline coordinated bis(naphthalene-2,3-diolato)-germanium complex reported recently by Syroeshkin,[20] complex **1**·2(phen)·2(THF) has monomeric structure, and no dimeric or polymeric association was observed. The germanium centre is coordinated by six oxygen atoms in PLs to form slightly distorted octahedral configuration (the *anti*-O–Ge–O bond angles are 170.34–173.46°). The Ge–O bond lengths range from 1.889 Å [Ge(1)–O(3)] to 1.906 Å [Ge(1)–O(2)], and their values

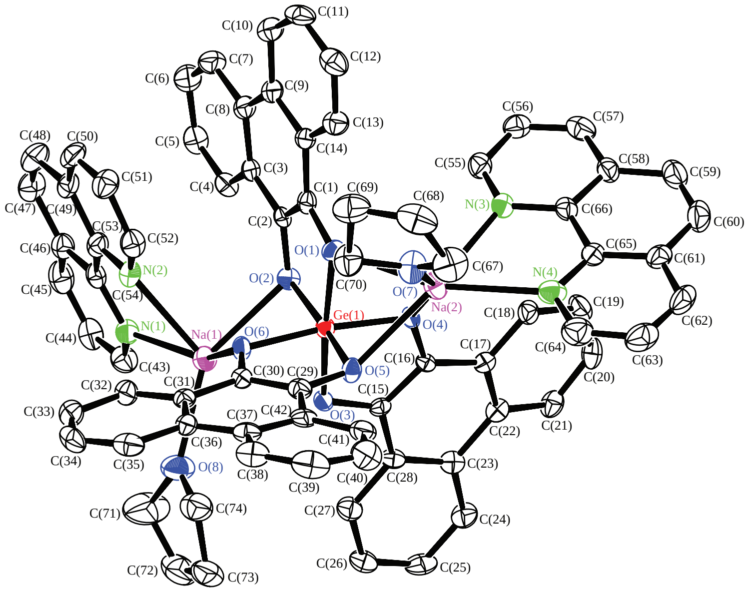

Figure 4 Molecular structure of **1**·2(phen)·(THF). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge(1)–O(1) 1.897(2), Ge(1)–O(2) 1.906(2), Ge(1)–O(3) 1.889(2), Ge(1)–O(4) 1.890(2), Ge(1)–O(5) 1.904(2), Ge(1)–O(6) 1.893(2); O(1)–Ge(1)–O(2) 86.93(10), O(1)–Ge(1)–O(3) 173.46(10), O(1)–Ge(1)–O(4) 87.44(10), O(1)–Ge(1)–O(5) 87.06(10), O(1)–Ge(1)–O(6) 98.03(10), O(2)–Ge(1)–O(5) 170.34(11), O(4)–Ge(1)–O(6) 173.26(10).

are comparable to those in **1**·2(PQ)·(DMSO)·3(MeOH). Each sodium atom is coordinated by two nitrogen atoms of phenanthroline, one oxygen atom of THF, and three oxygen atoms of PLs. Interestingly, the phenanthrene ring [C(1)–C(14)] and a phenanthroline ring [C(43)–C(52)] are relatively close to each other. The closest interatomic distance of C(4)–C(53) is 3.167 Å, which is less than the sum of the corresponding van der Waals radii (3.40 Å).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.01.003.

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Received: 27th August 2021; Com. 21/6663