Barium complex with 2,2,6,6-tetramethylheptane-3,5-dione and 4,7-diphenyl-1,10-phenanthroline

Nataliya P. Kuz'mina,*[a] Irina E. Soboleva,[a] Valerii A. Ketsko[b] and Sergei I. Troyanov[a]

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119899 Moscow, Russian Federation. Fax:+7 095 939 0283*
[b] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 117907 Moscow, Russian Federation. Fax: +7 095 954 1279*

The interaction between $[Ba(dpm)]_4$ and anhydrous B-phen (mole ratio 1:2) in benzene leads to the formation of the new mixed-ligand complex $Ba(dpm)_2(B\text{-}phen)_2\cdot C_6H_6$, which consists of the mononuclear molecules $Ba(dpm)_2(B\text{-}phen)_2$ with the *cis* arrangement of B-phen ligands involved in both intermolecular and intramolecular π–π interactions.

In recent years, interest in the synthesis and crystal structure of volatile barium β-diketonates has been associated with their intensive use as volatile precursors in the metal-organic chemical vapour deposition (MOCVD) of barium-containing thin films.[1] The use of barium β-diketonates as MOCVD precursors is complicated by low volatility and thermal stability of these complexes, which result from their oligomeric structure.[2] For example, the well-known and widely used barium complex with 2,2,6,6-tetramethylheptane-3,5-dione (dipivaloylmethane, Hdpm) exhibits the tetranuclear structure $[Ba(dpm)_2]_4$,[3] and its vapour consists of trinuclear and tetranuclear species.[4,5] The interaction of $[Ba(dpm)_2]_4$ with neutral donor ligands Q (Lewis bases) leads to the formation of mononuclear mixed-ligand complexes $[Ba(dpm)_2(Q)_n]$,[2] where $n = 1$, Q = tetraglyme[6] or $n = 2$, Q = 1,10-phenanthroline (phen).[7] When heated, the $[Ba(dpm)_2(Q)_n]$ complexes decompose with the elimination of more highly volatile Q ligands and with the formation of non-volatile parent $[Ba(dpm)_2]_4$. It is rather difficult to synthesise a $[Ba(dpm)_2(Q)_n]$ complex that can undergo sublimation without decomposition because of the low Lewis acidity of $Ba(dpm)_2$. We suggested that the addition of a low-volatility ligand Q to $[Ba(dpm)_2]_4$ can result in higher thermal stability of $[Ba(dpm)_2(Q)_n]$. In this work, 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline, B-phen) is used as this neutral ligand Q, whose volatility is comparable to that of $[Ba(dpm)_2]_4$. Bathophenanthroline, as well as $[Ba(dpm)_2]_4$, evaporates in a temperature range of 220–240 °C at 0.1 Torr. Its complex with $Ba(dpm)_2$ was synthesised and examined using different techniques including X-ray diffraction analysis.

The interaction between $[Ba(dpm)]_4$ and anhydrous B-phen (mole ratio 1:2) in benzene resulted in mixed-ligand complex $Ba(dpm)_2(B\text{-}phen)_2\cdot C_6H_6$ **1**.[†] This procedure gave a white crystalline precipitate, which exhibited X-ray diffraction patterns consistent with those calculated for **1**. The thermal analysis showed that C_6H_6 molecules were removed in the temperature range 50–100 °C to form $Ba(dpm)_2(B\text{-}phen)_2$, as was confirmed by elemental analysis.[‡]

An X-ray examination of **1** showed that it consists of the mononuclear molecules $Ba(dpm)_2(B\text{-}phen)_2$.[§] The C_6H_6 molecules are situated in cavities and do not take part in coordination. The central Ba atom, lying on the twofold axis, coordinates four oxygen atoms of the two dpm ligands and four nitrogen atoms of the B-phen molecules [Figure 1(*a*)]. All of the ligand donor atoms are involved in chelate rings. The coordination polyhedron of barium is a distorted tetragonal antiprism, as in the case of the known $Ba(dpm)_2(phen)_2$ complex.[7] In **1**, The Ba–O and Ba–N bond lengths [Ba–O(1) 2.683(5), Ba–O(2) 2.625(5), Ba–N(1) 2.969(5) and Ba–N(2) 2.986(5) Å] and the angles O(1)–Ba–O(2) and N(1)–Ba–N(2) [65.3(2) and 54.0(2)°, respectively] are close to the corresponding values in $Ba(dpm)_2(phen)_2$.[7]

The $Ba(dpm)_2(B\text{-}phen)_2$ and $Ba(dpm)_2(phen)_2$ molecules differ in the composition of neutral ligands. Bathophenanthroline is a phenanthroline derivative in which two H atoms are replaced by phenyl groups. This difference influences the mutual arrangement of ligands and the molecular packing mode in the crystal structure. The phen ligands in $Ba(dpm)_2(phen)_2$ are in the *trans*-position and participate in intermolecular π–π interactions, forming infinite chains with a phen–phen distance of 3.46 Å.[7] The characteristic feature of a $Ba(dpm)_2(B\text{-}phen)_2$ molecule is the *cis*-position of two B-phen ligands and the participation of their heterocyclic aromatic systems in both intermolecular and intramolecular π–π interactions [Figure 1(*b*)]. The B-phen ligands from different molecules are stacked in parallel planes at a distance of 3.43–3.45 Å, forming chains aligned in the *z* direction.

On heating in a vacuum, complex **1** eliminated a C_6H_6 molecule at a temperature lower than 75 °C. Within the temperature range 165–500 °C, the weight loss occurred in two steps. The first step (165–260 °C, a weight loss of 45%) corresponded to the evaporation of $Ba(dpm)_2(B\text{-}phen)_2$, as was confirmed by the elemental analysis and ^{1}H NMR data obtained for the sublimate.[¶] At the second step (260–500 °C), thermolysis of the organic moieties of the complex was observed. The total weight

---

[†] Synthesis of **1**: $Ba(dpm)_2$ (0.956 g, 0.19 mmol) and B-phen (1.262 g, 0.38 mmol) were suspended in benzene (30 ml), and the reaction mixture was heated at reflux with stirring until complete dissolution of the reactants. On cooling the solution, colourless prismatic crystals were formed; they were dried in a vacuum at room temperature (yield 80%). The solubility in C_6H_6 is 1.26 mmol dm^{-3}. ^{1}H NMR for $BaC_{70}H_{70}N_4O_4$ (25 °C, C_6D_6) δ: 9.67 and 9.66 (4H), 7.52 (4H), 7.20 (20H), 7.16 and 7.13 (4H), 5.98 (2H), 1.41 (36H). IR spectra were measured on a UR-20 spectrometer. IR (Nujol and hexachlorobutadiene mulls, ν/cm^{-1}): 2855 and 2945 (C–H), 1560 and 1570 (C=O), 1530 (C=C), 850 (C–CMe_3), 1265 (C–CMe_3), 1650, 1655, 705, 740, 765, 790, 850, 940 and 980 (B-phen). Found (%): C, 73.40; H, 6.22; N, 4.44; Ba, 10.8. Calc. for $BaC_{70}H_{70}N_4O_4\cdot C_6H_6$ (%): C, 73.25; H, 6.10; N, 4.50; Ba, 11.00.

[‡] Found (%): C, 72.05; H, 6.14; N, 4.81; Ba, 11.8. Calc. for $BaC_{70}H_{70}N_4O_4$: C, 71.98; H, 6.00; N, 4.80; Ba, 11.74. Thermogravimetric analysis was performed on an OD-102 derivatograph in a nitrogen atmosphere at a heating rate of 5 K min^{-1}. After the elimination of C_6H_6, three-step thermal decomposition took place in the temperature range 210–500 °C with the total weight loss 75%.

[§] *Single-crystal X-ray diffraction analysis.* A single crystal (0.2×0.2×0.3 mm) of **1** suitable for an X-ray diffraction examination was selected from the product obtained by slow crystallisation from a benzene solution of **1** in an evacuated ampoule. Crystal data for **1**: $C_{76}H_{76}N_4O_4Ba$, $M = 1246.75$, orthorhombic, space group *Pbcn*, $a = 13.933(5)$ Å, $b = 30.180(10)$ Å, $c = 16.264(6)$ Å, $V = 6868(6)$ Å^3, $Z = 4$, $d_{calc} = 1.206$ g cm^{-3}, $\mu = 6.28$ cm^{-1}. The data were collected on an Enraf-Nonius CAD 4 diffractometer ($2 < \theta < 21.6°$, monochromatic MoKα radiation, $\lambda = 0.7107$ Å, $T = 293$ K); 6322 unique reflections were measured, and 3453 reflections were used without absorption correction in calculations with the SHELX-97 program package. The structure was solved using a combination of direct and Fourier methods and refined by the full-matrix least-squares technique with the anisotropic thermal parameters for all non-hydrogen atoms. H atoms were placed in calculated positions. The final *R* values were $R_1 = 0.0569$ and $wR_2 = 0.1267$. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, 1999, Issue 1. Any request to the CCDC should quote the full literature citation and the reference number 1135/47.

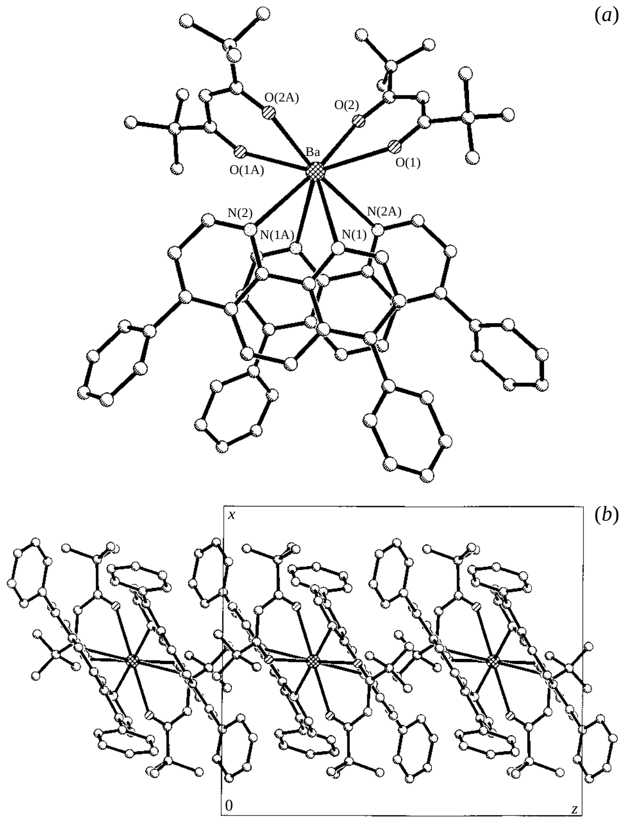

Figure 1 (*a*) Molecular structure of $Ba(dpm)_2(B\text{-}phen)_2$ and (*b*) a fragment of the molecular packing in the crystal structure.

loss for **1** was 92%. The vacuum sublimation experiments corroborated that $Ba(dpm)_2(B\text{-}phen)_2$ evaporated congruently in the temperature range 200–250 °C; however, the evaporation was very slow. At temperatures higher than 250 °C, the complex underwent thermal decomposition. The behaviour of the $Ba(dpm)_2(phen)_2$ complex on heating was different from that of **1**. The former was incongruently transformed into a vapour phase. Phenanthroline molecules were eliminated at 120–180 °C; next, the barium complex with dipivaloylmethane evaporated at higher temperatures (180–220 °C).[7] The difference between $Ba(dpm)_2(B\text{-}phen)_2$ and $Ba(dpm)_2(phen)_2$ in volatility can be explained by special features of the crystal structures. For **1**, the enhanced thermal stability with respect to decomposition into B-phen and $Ba(dpm)_2$ can be explained by the formation of a 'superligand' that consists of several B-phen ligands, which are strongly connected by intra- and intermolecular π–π interactions [Figure 1(*b*)].

Thus, our approach to the synthesis of thermally stable $Ba(dpm)_2(Q)_2$ compounds using low-volatility neutral ligands was successful. Compound **1** is the first example of a $Ba(dpm)_2(Q)_2$ complex that undergoes congruent evaporation; however, unfortunately, the volatility of this compound was found to be rather low.

This work was supported by the Russian Foundation for Basic Research (grant no. 96-03-32937a).

References

1 M. Tiita and L. Niinisto, *Chemical Vapour Deposition*, 1997, **3**, 167.
2 A. Drozdov and S. I. Troyanov, *Main Group Metal Chemistry*, 1996, 547.
3 A. Drozdov and S. I. Troyanov, *Polyhedron*, 1992, **3**, 2877.
4 A. S. Alikhanyan, I. P. Malkerova, N. P. Kuz'mina, V. K. Ivanov and A. R. Kaul', *Zh. Neorg. Khim.*, 1994, **39**, 1534 (*Russ. J. Inorg. Chem.*, 1994, **39**, 1465).
5 N. I. Giricheva, N. A. Isakova, N. P. Kuz'mina, G. V. Girichev, V. M. Petrov and A. R. Kaul', *Zh. Neorg. Khim.*, 1996, **41**, 1523 (*Russ. J. Inorg. Chem.*, 1996, **41**, 1457).
6 R. G. Gardiner, D. W. Brown, P. S. Kirlin and A. L. Rheingold., *Chem. Mater.*, 1991, **3**, 1053.
7 N. Kuzmina, V. Ivanov, S. I. Troyanov and L. Martynenko, *J. Chem. Vap. Deposition*, 1994, **3**, 32.

Received: 21st January 1999; Com. 99/1429

¶ *Thermogravimetric analysis* was performed on a T-7000 Sinku-Riko thermal analyser in a vacuum (0.01 Torr) at a heating rate of 10 K min^{-1}. *Vacuum sublimation*: samples of **1** were evaporated in glass tubes at a pressure of 0.01 Torr; the temperature range was 180–220 °C; the sample weight was 50 mg. The total weight loss of a sample was determined by gravimetry. All sublimate fractions collected in the course of isothermal heating within the range 200–245 °C exhibited spectrochemical and elemental analysis data that correspond to $BaC_{70}H_{70}N_4O_4$.