Inorganica Chimica Acta, *166* (1989) 31–33

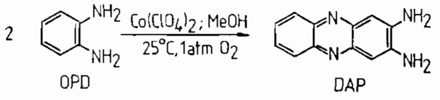
Formation of Bis(*o*-benzosemiquinonediiminato)-cobalt(III) Derivatives by Oxidation of *o*-Phenylenediaminecobalt(II) Complexes with O_2

SÁNDOR NÉMETH, LÁSZLÓ I. SIMÁNDI*,
GYULA ARGAY and ALAJOS KÁLMÁN

Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1525 Budapest, P. O. Box 17 (Hungary)

(Received May 31, 1989; revised August 20, 1989)

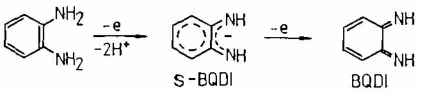
We have reported earlier [1] that cobalt(II) salts catalyze the oxidation of *o*-phenylenediamine (OPD) to 2,3-diaminophenazine (DAP)



(1)

Upon addition of Ph_3P in a 5-fold excess over cobalt(II), the catalytic process afforded Ph_3PO, but after consumption of about 2/3 of the added Ph_3P, the process reverted gradually to reaction (1). Toward the end of the Ph_3P oxidation stage, a green compound (complex **A**) gradually precipitated, which is related to the intermediate of the catalytic process; *viz.* the *o*-benzoquinonediimine (BQDI) complex of cobalt(II). We now report the isolation and structure determination of this compound as well as the synthesis and characterization of its Ph_3As and Ph_3Sb analogues.

Under the conditions when the green complex is obtained in maximum yield, the formation of DAP cannot be observed. Consequently, the complex contains some oxidized form of OPD in a lower oxidation state than DAP. An earlier report [2] postulated that OPD is oxidized to BQDI via the intermediate stage of *o*-benzosemiquinonediimine (s-BQDI)



which then transforms to DAP via a complex route. BQDI has never been prepared in the free state and s-BQDI is too reactive to be isolated. However, both can be stabilized by coordination to transition metal ions. There has been considerable interest in such complexes [3–7] because of their unusual chemical and structural properties imparted by the 'non-innocent' ligands involved [6]. Redox lability and oxygen sensitivity often complicate the synthesis and affect the products obtained [4, 7, 8].

Experimental

Crystal data of A

An Enraf-Nonius CAD-4 diffractometer with graphite monochromated Cu Kα radiation was used ($\lambda = 1.54184$ Å) with a scintillation counter (ω–2θ scan in the range $3° < 2\theta < 150°$; $T = 296$ K) and empirical absorption correction. Crystal data for $C_{30}H_{27}N_4PCo \cdot ClO_4 \cdot 0.5C_6H_6$ are: $M = 671.99$, monoclinic, space group $P2_{1/n}$; $a = 13.069(2)$, $b = 16.720(2)$, $c = 14.391(3)$ Å; $\beta = 96.58(1)°$, $V = 3123.94$ Å^3, $Z = 4$, $D_c = 1.429$ g cm^{-3}; μ(Cu Kα) = 61.67 cm^{-1}; crystal dimensions 0.28 × 0.11 × 0.60 mm. A total of 5355 reflections gave $R_{(\mathrm{Rn})} = 0.072$ (0.088) for 3731 reflections with $F^2 > 2.0\,\sigma\,(F^2)$ (398 variables). Hydrogens at N atoms could not be localised in a difference electron density map. Other H atoms were included in calculated positions with isotropic temperature factors $B_{iH} = B_{iX} + 1$ Å, where X = C or N; all other atoms were refined anisotropically. Calculations were performed by the Enraf-Nonius program system [10] run on a PDP-11/34 minicomputer.

[Co^{III}(s-BQDI)$_2$(Ph_3P)]$ClO_4 \cdot 0.5C_6H_6$ (Complex A)

To a solution of 1.08 g (0.01 mol) OPD and 2.62 g (0.01 mol) Ph_3P (of which about 20% remains undissolved) in MeOH was added 1.83 g (0.005 mol) $Co(ClO_4)_2 \cdot 6H_2O$ under pure O_2. The absorption of O_2 ceased after about 10 h (total of *c.* 150 cm^3 STP). The fine black powder precipitated was washed with benzene (yield 1.6 g; 51%). The crude product was recrystallized from MeOH/benzene, giving fine black crystals 0.5–1.5 mm in size, suitable for X-ray diffraction. IR spectrum (cm^{-1}, relative intensities in parentheses): 3265(7), 3025(2), 1530(7), 1475(4), 1460(2), 1443(8), 1435(6), 1380(2), 1342(10), 1200(4), 1140(8), 1075(9, two shoulders), 825(4), 751(sh), 748(4), 740(5), 690(6), 685(7), 630(8). ^{1}H NMR (ppm, in $CDCl_3$/DMSO): 6.85–7.45 (multiplet, 23 H); 11.64 (broad s, 4H, slowly exchangeable with D_2O). *Anal.* Found: C, 58.28; H, 4.41; N, 8.17; P, 5.28; Cl, 5.87; Co, 8.90. Calcd.: C, 58.97; H, 4.46; N, 8.33; P. 4.61; Cl, 5.28; Co, 8.78%.

[Co^{III}(s-BQDI)$_2$(Ph_3As)]ClO_4 (Complex B)

This was made by the same procedure as that for synthesizing **A**, using 3.06 g Ph_3As and a 20-min reaction time (yield 1.7 g of dark powder, 55%). *Anal.* Found: C, 52.79; H, 4.33; N, 8.13; Cl, 5.38. Calc.: C, 53.23; H, 4.02; N, 8.28; Cl, 5.24%. IR spectrum was essentially identical to that of **A**. ^{1}H NMR ($CDCl_3$; δ in ppm): multiplet at 6.65–7.45 (23 H); 11.04 (2, 4H), broad, D_2O exchangeable.

0020-1693/89/$3.50

[Co^{III}(s-BQDI)$_2$(Ph_3Sb)]ClO_4 (Complex C)

This was prepared by the same procedure as for **A** and **B**, using 3.53 g Ph_3Sb (reaction time 1 h; yield 1.6 g dark powder; 40%). *Anal.* Found: C, 49.00; H, 3.47; N, 7.60; Cl, 4.57; Co, 8.0. Calc.: C, 49.75; H, 3.73; N, 7.74; Cl, 4.90; Co, 8.15%. IR spectrum was essentially identical to those of **A** and **B**. ^1H NMR ($CDCl_3$; δ ppm): 6.60–7.40 (multiplet, 23H), 11.20 (s, 2H; rapid D_2O exchange).

Results and Discussion

The novel synthetic method reported here is based on the remarkable fact that O_2-oxidation of OPD in the presence of cobalt(II) perchlorate and Ph_3X (X = P, As, Sb) stops at the s-BQDI stage.

Upon exposure to pure O_2 of a MeOH solution containing 5×10^{-2} M $Co(ClO_4)_2 \cdot 6H_2O$ and a twofold excess of each OPD and Ph_3P, a fine black powder (complex **A**) separates after *c.* 10 h. Up to this time the reaction mixture has absorbed a total of 0.75 mole O_2/mole Co. The IR spectrum of **A** reveals the presence of Ph_3P in the coordination sphere, showing characteristic bands at 1475, 1445, 1340, 748, 740 and 690 cm^{-1}. GLC analyses gave a Ph_3P/Co ratio of (1.0 ± 0.03). The presence of ClO_4^- is obvious from the broad, intense band around 1075 cm^{-1}. The intense aromatic skeletal vibrations of OPD at 1635, 1595 and 1278 cm^{-1}, and its $-NH_2$ bands at 3320 and 3340 cm^{-1} are absent. The sharp, intense NH band at 3265 cm^{-1} and the new bands at 1529, 1460, 1380 and 1340 cm^{-1} (the latter strongly intensified with respect to that of Ph_3P) strongly indicate that the coordinated OPD has been oxidized to s-BQDI or BQDI. The appropriate bands in the spectrum of [$Fe(CN)_4$(BQDI)] are at 1520, 1450 and 1375 cm^{-1} [4]. ^1H NMR spectra reveal a broad singlet at 11.64 ppm (4H), which is slowly exchangeable with D_2O. This is similar to the 11.08 ppm reported for the product obtained by reacting [Co(OPD)(s-BQDI)$_2$]PF_6 with Ph_3P [7]. Bands appear at 709 ('diimine band') and 510 nm in the visible spectrum. The compound is ESR silent.

The structure of **A** has been determined by X-ray diffraction (Fig. 1). According to the X-ray results, compound **A** contains 2 identical equatorial ligands. The net 1^+ charge of the complex ion requires that both ligands carry a 1^- formal charge and the central ion be cobalt(III). Owing to the non-innocent nature of s-BQDI ligands, significant cobalt(II) character may prevail and contribute to the stability of the penta-coordinate structure. In combination with elemental analysis, we deduce the formula [Co^{III}(s-BQDI)$_2Ph_3P$]$ClO_4 \cdot 0.5C_6H_6$ for **A**. (The 0.5 mole of benzene is due to crystallization from MeOH/benzene.)

The coordination polyhedron of **A** is a square pyramid with Ph_3P in the axial position. The cobalt atom resides 0.32 Å above the basal plane. The perchlorate ion is not within bonding distance (5 Å) to the cobalt, its role being that of a spacer. In solution the 6th coordination site is also occupied by a solvent or ligand molecule.

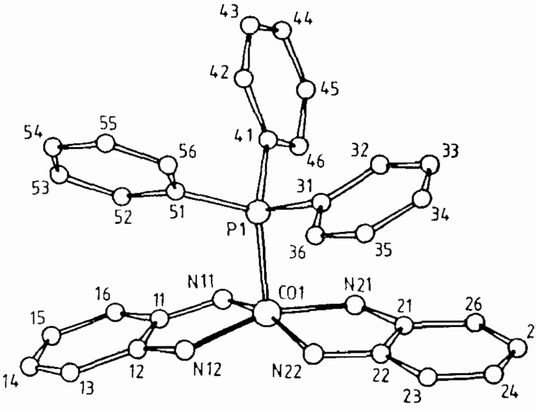


Fig. 1. Perspective view of molecule A, showing the numbering of atoms. The base numbers are for carbon atoms; hydrogens are not shown. Selected bond distances (Å): Co(1)–P(1), 2.231(2); Co(1)–N(11), 1.873(6); Co(1)–N(12), 1.864(7); Co(1)–N(21), 1.878(6); Co(1)–N(22), 1.861(7); shortest Co(1)–O(11), 4.227 (to perchlorate ion); N(11)–C(11), 1.337(10); N(12)–C(12), 1.334(11); N(21)–C(21), 1.339(11); N(22)–C(22), 1.332(10); C(11)–C(12), 1.438(11); C(11)–C(16), 1.431(12); C(12)–C(13), 1.431(13); C(13)–C(14), 1.352(14); C(14)–C(15), 1.439(16); C(15)–C(16), 1.362(14). Selected bond angles (°): N(11)–Co(1)–N(22), 161.0(5); N(12)–Co(1)–N(21), 159.9(5); N(11)–Co(1)–N(12), 83.7(5); N(21)–Co(1)–N(22), 83.6(5); N(12)–Co(1)–N(22), 92.0(5); N(11)–Co(1)–N(21), 94.2(5); P(1)–Co(1)–N(11), 101.4(4); P(1)–Co(1)–N(22), 97.5(4).

The average C$\cdots$N bond distance of 1.335 Å in **A** is slightly longer than the C=N distance (1.300 Å) in the [$Fe(BQDI)_3$]$^{2+}$ ion [9]. It agrees very well with the average C$\cdots$N bond length of 1.337 Å observed in the equatorial ligands of the compound described earlier as [Co(s-BQDI)(BQDI)$_2$]$^+$ [8]. This complex was later correctly reformulated as [Co^{III}(OPD)(s-BQDI)$_2$]$^+$, with OPD as a unidentate axial ligand [9].

We have found that similar complexes are formed when instead of Ph_3P, we use Ph_3As or Ph_3Sb. These complexes have been characterised by elemental analysis, IR and ^1H NMR spectroscopy.

The procedure described can be extended to other s-BQDI complexes with different axial ligands.

Supplementary Material

The atomic coordinates and vibrational parameters for this work are available on request from the Director of the Cambridge Crystallographic Data

Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation of this communication.

Acknowledgement

Financial support by the Hungarian Research Fund (Grant 1036) is gratefully acknowledged.

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