

Preliminary communication

The cobaloximes *trans*-bis(dimethylglyoxime)(R)Co^{III}, R = *n*-C₁₄H₂₉ or *n*-C₁₅H₃₁. Surprising ambiphilic nature observed in the molecular packing of the longest *n*-alkyl organometallic compound to be structurally characterized

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Abstract

The cobaloximes, *trans*-bis(dimethylglyoxime)(pyridine)(R)cobalt(III) where R = (*n*-tetradecyl) or (*n*-pentadecyl) have been synthesized and fully characterized. The crystal structure of the *n*-tetradecyl compound has been determined and found to be analogous to that of common ambiphilic molecules.

Keywords: Cobalt; Cobaloximes; Ambiphilicity; Crystal structure; Hydrogen bonding

Cobaloximes, the trivial name for complexes containing the bis(dimethylglyoximate)cobalt unit, Co(DH)₂, have been extensively studied as model systems in the elucidation of the mechanism of action of the vitamin B₁₂ coenzyme [1]. Organocobaloximes, prepared by the reaction of cobaloxime chloride, [(py)Co(DH)₂Cl], and an alkyl halide under reducing conditions, are photochemically and air stable at room temperature for relatively long periods of time. These compounds commonly give well-formed crystals, and this has allowed the crystallographic determination of many compounds having this general structure [2].

In this report we describe the synthesis and characterization of [(py)Co(DH)₂(*n*-C₁₄H₂₉)] (1) and [(py)Co(DH)₂(*n*-C₁₅H₃₁)] (2). The crystal structure of the longest organometallic straight-chain alkyl compound, (1), is also presented with a comment on its interesting crystal packing. Numerous *n*-butyl organometallic compounds have been structurally characterized [3] and the longest chains reported before this work were found for the complexes [{η⁶-C₅Me₅}Fe(CO)₂(*n*-C₅H₁₁)] [4] (where Me = methyl) and recently Ph₄As[(*n*-C₆H₁₃)Ir(CO)₂I₃] [5].

Compounds (1) and (2) [6] were prepared by standard procedures [7], involving reaction of [(py)Co(DH)₂Cl] with the appropriate alkyl bromide, to give good yields (85% and 82% respectively) of orange-brown crystals of satisfactory elemental analysis. Compound (1) gave good crystals for an X-ray diffraction study, but attempts to obtain satisfactory crystals of (2) have been unsuccessful [8].

Data collection: Compound (1) was crystallized from methanol at -15°C (in the dark). A crystal of size 0.13 × 0.13 × 0.22 mm was used. Space group P 2₁/c, *a* = 22.75(2), *b* = 8.298(2), *c* = 16.772(9) Å, β = 106.85(5)° Z = 4 formula units of C₂₇H₄₈CoN₅O₄; D_c 1.24 Mg m⁻³ (293 K). Intensity data were collected on an Enraf Nonius CAD4 diffractometer with graphite-monochromated Mo K_α radiation (λ = 0.7107 Å), μ = 0.6 mm⁻¹. Lattice parameters were obtained by least squares refinement of the setting angles of 24 reflections with 17 ≤ θ ≤ 16°. The ω-2θ scan method and a scan width of (0.80 + 0.35 tan θ)° were used. Data were corrected for background, scan speed, Lorentz and polarization effects; an empirical absorption correction [9] was applied, transmission factors 0.69 to 1.00.

The cobalt atom was located using the Patterson function while the remainder of the structure was solved by difference Fourier methods using SHELXL-93

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[10]. Refinement on F^2 converged to a weighted R value (wR2) of 0.2156 for all 5288 unique reflections. The conventional R factor was 0.087 for 1673 reflections with $I > 2\sigma(I)$. The final model included anisotropic refinement (based on F^2) of all non-hydrogen atoms and geometric placement of hydrogens, except the hydroxyl hydrogens, which were located in a difference Fourier map and allowed to refine independently, but at a constrained O–H bond distance of 0.82 Å.

Crystal and molecular structure: Fig. 1 shows a perspective view of the molecule, which consists of a discrete $(py)Co(DH)_2(n-C_{14}H_{29})$ unit. The four nitrogen atoms of the equatorial DH ligands are coplanar to within ± 0.003 Å. The cobalt atom is displaced from this plane by 0.023(4) Å, towards the pyridine. The pyridine ring is planar with a mean deviation from the plane of 0.009 Å. The tetradecane chain adopts an extended, staggered conformation with C–C lengths between 1.423(13) and 1.517(13) Å and C–C–C angles between 116(1) and 121(1)°. The bond Co(1)–C(6) is not perpendicular to the equatorial plane. N(2)–Co(1)–C(6) is 87.4(4)° and N(3)–Co(1)–C(6) is 86.7(3)°. The corresponding opposite angles N(4)–Co(1)–C(6) and N(1)–Co(1)–C(6) are 91.4(3) and 91.7(3)° respectively. The Co–C bond length (1.97(1) Å) and other bond lengths and angles are within expected ranges for published cobaloximes structures. The intra-molecular hydrogen bonds connected to O(3A) and O(1A) are also similar to those in previously reported structures.

The most interesting aspect of the structure is the molecular packing in the crystal. The packing is deter-

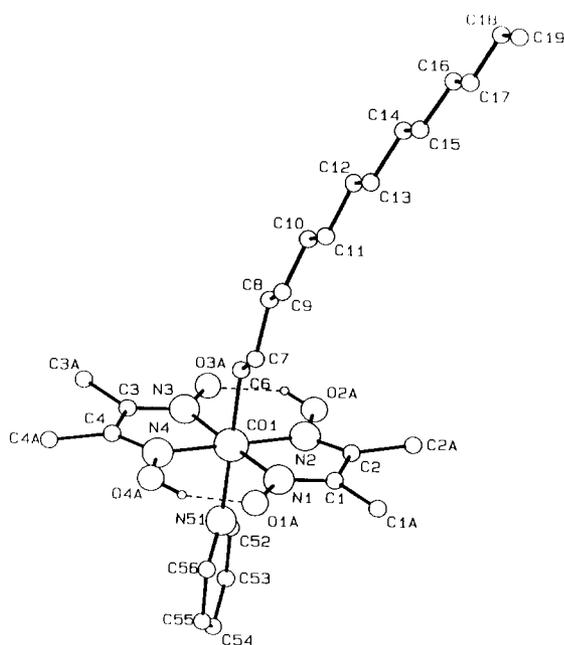


Fig. 1. Molecular structure of (I).

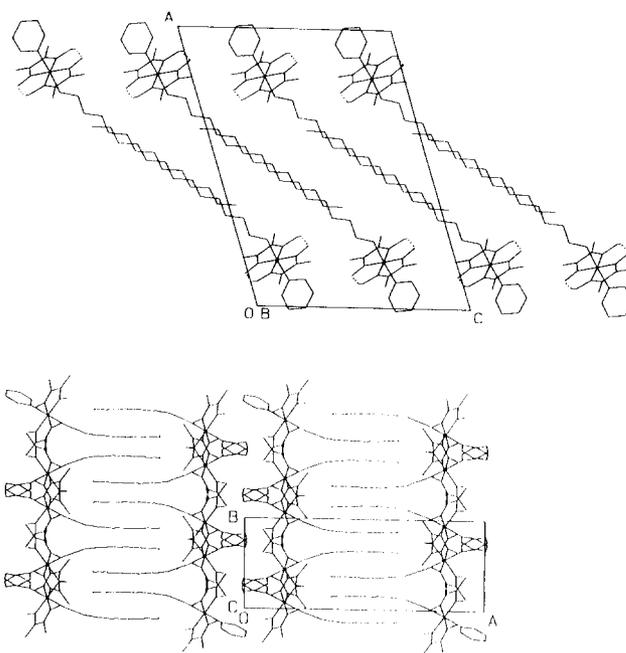


Fig. 2. Perspective view along (a) [010] and (b) [001] (the boxed regions indicate the unit cell).

mined chiefly by van der Waals forces, no intermolecular hydrogen bonds being detected. The molecules pack in columns parallel to [010] and [001] with interleaving tetradecane chains, as shown in Fig. 2. This sort of arrangement is reminiscent of surfactant molecules; e.g. the tetraalkylammonium salt $[CH_3-(CH_2)_{15}N(CH_3)_3]Br$ [11], where their amphiphilic nature induces alternating layers of hydrophilic heads and hydrophobic alkyl tails. The relative hydrophilicity of the cobaloxime unit (the “head”) is illustrated by the fact that $(py)Co(DH)_2Cl$ is sparingly soluble in water [7]. Complexes which have longer and more complex alkyl groups are totally insoluble in water. The nature of the alkyl group dominates the solubility character to such an extent that the title compound is in fact sparingly soluble in hexane!

Since the packing is analogous to that of surfactant molecules, further experiments are underway to determine whether the solution behaviour of these cobaloximes mimic that of common surfactants, e.g. in micelle formation [12].

Acknowledgements

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References and notes

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- [6] Compound (1): ^1H NMR (CDCl_3) δ 8.58(d, 2H, *o*-H of py); δ 7.69(t, 2H, *m*-H of py); δ 7.29(t, 1H, *p*-H of py); δ 2.11(s, 12H, CH_3 of DH); δ 1.63(m, 2H, Co-CH_2-); δ 1.24(m, 24H, alkyl- CH_2-); δ 0.87(t, 3H, terminal- CH_3). ^{13}C NMR δ 149.99(*o*-CH of py); δ 148.98(C=N); δ 137.28(*p*-CH of py); δ 125.08(*m*-CH of py); δ 31.91, 30.74, 30.68, 29.68, 29.46, 29.34($-\text{CH}_2-$); δ 22.67($-\text{CH}_2\text{CH}_3$); δ 14.09($-\text{CH}_3$); δ 11.95($-\text{CH}_3$ of DH). Compound (2): As for (1) except ^1H NMR δ 1.24(m, 26H, alkyl- CH_2-).
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