New Stable Dinuclear Organocobalt Complexes with a Tridentate Imino−Oxime Ligand

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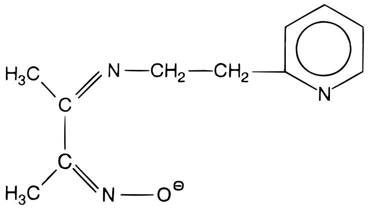
For many years, tetradentate imino−oxime and Schiff base ligands have been shown to stabilize the Co−alkyl σ-bond in octahedral complexes, where they occupy the four equatorial positions.[1,2] For this reason, their organocobalt derivatives have been considered simple models of the vitamin B_{12} system, e.g. the well-known alkylcobaloximes $RCo(Hdmg)_2L$, where R = alkyl group, L = neutral Lewis base, and Hdmg = monoanion of dimethylglyoxime.[1] The stabilization of the Co−C bond in these complexes is believed to be due to the electron charge delocalization over the equatorial moiety, including the Co center.[3] To our knowledge, the only example in the literature of a tridentate ligand stabilizing the Co−C bond is represented by a Schiff base, namely *N*-(2-aminoethyl)-7-methylsalicylaldiminato,[4] while alkylcobalt complexes containing tridentate imino−oxime ligands have not been reported. Deprotonated imino−oxime ligands, such as 2-(2-X-ethyl)imino-3-butanone oximato (LE-py), for X = 2-pyridyl (see structure **I**), and LE-am, for X = NH_2, have been shown to act as tridentate ligands, coordinating metal ions of the first transition series through their N-donors, to form species with metal:ligand ratios of 1:2, as in $[Co^{III}(LE\text{-}py)_2]ClO_4$[5] (**1**) and $[Ni^{IV}(LE\text{-}am)_2](ClO_4)_2$,[6] and stabilizing the metal center in high oxidation state. In view of the outlined properties of the LE-py ligand, we were interested in investigating the possibility of obtaining stable alkylcobalt derivatives containing this ligand.



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The most effective method[7] to prepare alkylcobaloximes and other alkylcobalt complexes involves the *in situ* generation of the Co(I) species in aqueous methanolic solution at high pH and successive addition of the appropriate alkyl halide (eq 1).

$$[\mathrm{Co(III)}] \xrightarrow{2e\ (\mathrm{NaBH_4})} [\mathrm{Co(I)}]^- \xrightarrow{RX} [\mathrm{Co}]{-}\mathrm{R} + \mathrm{X}^- \qquad (1)$$

From compound **1**[8] and MeI as methylating agent, and with the above method, a red crystalline metalloorganic complex was obtained.[9] On the basis of the elemental analysis and X-ray single-crystal determination, the compound has been identified as the μ-hydroxo binuclear species $[(\mu\text{-OH})\{MeCo(LE\text{-}py)\}_2]ClO_4\cdot0.5H_2O$ (**2**). **[*Caution! Perchlorate salts of metal complexes with organic ligands are explosive.*]** Suitable crystals of **2** for X-ray analysis were obtained by slow diffusion of diethyl ether into a concentrated solution of the compound in methanol.

The crystal of **2** is built up by $[\{MeCo(LE\text{-}py)\}_2OH]^+$ cations, ClO_4^- anions, and H_2O hydration molecules.[10] The ORTEP drawing of one of the two crystallographically independent cations is depicted in Figure 1. The two cations have very similar geometry, with an approximate C_2 symmetry, the 2-fold axis passing through O3 and the midpoint of the two Co centers. Selected bond lengths and angles, reported in Figure 1, refer to one of the two cations with those relative to the other given in parentheses. Each Co(III) in the cation has a distorted octahedral geometry with the LE-py N donors occupying three equatorial positions in a *mer* arrangement; the bridging OH^- group occupies the fourth equatorial position. The axial positions are occupied by the Me and by the oxime O atom of the LE-py ligand coordinated to the other Co(III) (Figure 1). Thus, the LE-py ligand acts as tetradentate ligand, bridging the two cobalt ions through the O oxime atoms, in the same way as previously observed in the dinuclear copper(II) complexes $[Cu^{II}(LE\text{-}py)(MeCN)]_2(ClO_4)_2$[11] and $[Cu^{II}(LE\text{-}py)]_2(ClO_4)_2$.[12] The two metal centers, far apart at 3.055(2) and 3.058(2) Å in the two crystallographically independent cations, are triply-bridged by the OH and the two NO oxime groups. The Co(III)··Co(III) distances are close to those, ranging from 3.01 to 3.08 Å, reported in triply bridged coordination complexes, [(μ-

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(1) Randaccio, L.; Bresciani Pahor, N.; Zangrando, E.; Marzilli, L. G. *Chem. Soc. Rev.* **1989**, *18*, 225.

(2) Toscano, P. J.; Marzilli,L. G. *Prog. Inorg. Chem.* **1984**, *31*, 105.

(3) Bigotto, A.; Costa, G.; Mestroni, G.; Pellizer, G.; Puxeddu, A.; Reisenhofer, E.; Stefani, L.; Tauzher, G. *Inorg. Chim. Acta Rev.* **1970**, *4*, 41.

(4) (a) Levitin, I.; Sigan, A.; Kazarina, E.; Alexandrov, G.; Struchkov, Y.; Vol'pin, M. *J. Chem. Soc., Chem. Commun.* **1981**, 441. (b) Levitin, I. Ya.; Tsikalova, M. V.; Bakhmutov, V. I.; Yanovsky, A. I.; Struchkov, Yu.T.; Vol'pin, M. E. *J. Organomet. Chem.* **1987**, *330*, 161.

(5) Pajunen, A.; Pajunen, S. *Acta Crystallogr.* **1983**, *C39*, 852.

(6) (a) Singh, A. N.; Singh, R. P.; Mohanty, J. G.; Chakravorty, A. *Inorg. Chem.* **1977**, *16*, 2597. (b) Saarinen, H.; Korvenranta, J.; Näsäkkälä, E. *Acta Chem. Scand.* **1980**, *A34*, 443.

(7) Gupta, B. D.; Roy, S. *Inorg. Chim. Acta* **1988**, *146*, 209.

(8) Uhlig, E.; Schneider, D.; Hildebrandt, H. *Z. Anorg. Allg. Chem.* **1966**, *346*, 173.

(9) To a solution of **1** (0.51 g, 0.9 mmol) in 150 mL of methanol and NaOH (0.21 g, 5.2 mmol) in 15 mL of water, under inert atmosphere and stirring, was added $NaBH_4$ (0.34 g, 0.9 mmol), dissolved in 10 mL of water. When the solution assumed a dark brown color (heating is sometimes required to favor the reaction), 1 mL of CH_3I was added. In about 30 min, the intense coloration was discharged. Then the methanol was removed by a rotary evaporator, and the aqueous suspension of the product was extracted with CH_2Cl_2, reprecipitated with *n*-pentane, collected by filtration, and air-dried. The product was dissolved in water and reprecipitated as the perchlorate salt by addition of a concentrated solution of $NaClO_4$, collected by filtration, and dried under P_2O_5. Anal. Calcd for $C_{24}H_{35}N_6O_7ClCo_2$: C, 42.8; H, 5.2; N, 12.5. Found: C, 43.1; H, 5.3; N, 12.2. In the same way, using EtI as alkylating agent, the analogous ethyl derivative μ-OH[EtCo(LE-py)]$_2$ClO$_4$ (**3**) was obtained and characterized by elemental analysis. Anal. Calcd for $C_{26}H_{39}N_6O_7ClCo_2$: C, 44.5; H, 5.6; N, 12.0. Found: C, 44.5; H, 5.6; N, 12.3.

(10) Crystal data for **2**: formula $C_{24}H_{35}Co_2N_6O_3ClO_4\cdot0.5H_2O$, fw 681.8, monoclinic, space group $P2_1/c$ (No. 14), $a = 16.508(4)$ Å, $b = 15.965(4)$ Å, $c = 22.181(6)$ Å, $\beta = 96.50(4)°$, $V = 5808.1(8)$ Å^3, $Z = 8$, $\rho = 1.57$ g cm^{-3}, $T = 292$ K, $F(000) = 3177$. Anisotropic refinement of all non-hydrogen atoms (hydrogen atoms were not refined but were included at calculated positions in the final refinement) using 6947 data (730 variables) with $I_o > 3\sigma(I_o)$ from 14 041 unique data gave $R = 0.058$ and $R_w = 0.064$.

(11) Bertrand, J. A.; Smith, J. H.; Van Derveer, D. G. *Inorg. Chem.* **1977**, *16*, 1477.

(12) Nardin, G. Unpublished results.

S0020-1669(95)01407-8 CCC: $12.00

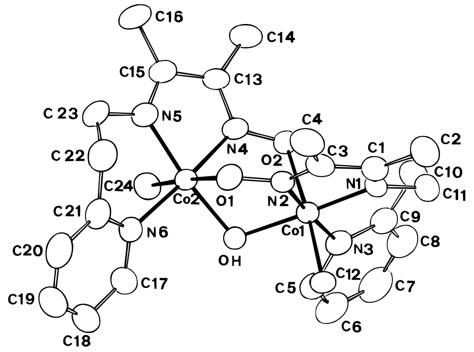

Figure 1. ORTEP drawing (thermal ellipsoid; 50% probability) and labeling scheme for one of the two crystollographically independent cations of $[(\mu\text{-OH})\{MeCo(LE\text{-}py)\}_2]ClO_4\cdot 0.5H_2O$. The ClO_4^- and H_2O species are omitted for clarity. Selected (a) bond distances (Å) and (b) bond angles (deg) follow, with the values for the other independent dimer in brackets. (a) Co1−O2 = 2.065(4) [2.058(4)], Co1−O3 = 1.917(4) [1.911(4)], Co1−N1 = 1.892(6) [1.886(6)], Co1−N2 = 1.873(5) [1.867(5)], Co1−N3 = 1.980(6) [1.972(5)], Co1−C12 = 1.961(7) [1.969(7)], Co2−O1 = 2.067(5) [2.035(5)], Co2−O3 = 1.911(4) [1.909(4)], Co2−N4 = 1.876(5) [1.873(6)], Co2−N5 = 1.963(6) [1.889(5)], Co2−N6 = 1.963(6) [1.964(6)], Co2−C24 = 1.982(7) [1.968(8)], O1−N2 = 1.325(7) [1.311(7)], O2−N4 = 1.316(7) [1.318(7)]. (b) Co2−O1−N2 = 107.9(3) [108.8(3)], Co1−O2−N4 = 107.7(3) [108.0(4)] Co1−O3−Co2 = 105.9(2) [106.4(2)], Co1−N2−O1 = 122.2(4) [122.8(4)], Co2−N4−O2 = 122.7(4) [122.5(4)].

$OH)\{Co_2(Hdmg)_3(H_2dmg)\}]^{2+}$,[13a] $[(\mu\text{-O})\{Co(Hdmg)_2\}_2]$,[13b] and $[(\mu\text{-O})\{Co_2(Hdmg)_2(dmg)_2\}OH]^{3-}$,[13c] which have the same Co(X,NO,ON)Co core with X = OH^- or O^{2-}. The Co1−C and Co2−C distances are 1.961(7) [1.969(7)] and 1.982(7) [1.968(8)] Å, respectively, very close to the value of 1.990(5) Å reported for the Co−C bond length in $MeCo(Hdmg)_2OH_2$.[14] Similarly, the Co−O(oxime) bond length (mean value 2.056(5) Å) is very close to that of Co−OH_2 (2.058(3) Å) in $MeCo(Hdmg)_2(H_2O)$.[14] These observations suggest that the two axial bonds are scarcely influenced by the nature of the other surrounding ligands. On the other hand, the Co−O(oxime) bond length is significantly longer with respect to those, ranging from 1.86 to 1.97 Å, found in the similar triply bridged complexes,[13] where O is *trans* to the N(oxime) atom. This is consistent with the large *trans* influence exerted by the Me group.

The reaction of the formation of **2** is characterized by sharp chromatic variations, the orange solution of **1** becoming dark brown after reduction with $NaBH_4$ and turning red after the addition of the alkyl iodide. These chromatic changes are similar to those observed during the synthesis of organocobaloximes, suggesting that also in the present case the process involves the formation of a Co(I) nucleophile. This species can be recognized by its oxygen sensitivity and the dark-brown color, which is due to ligand-field transitions in the visible region, where **1** does not exhibit any absorption. In fact, the spectrum of the Co(I) species is characterized by the presence of two strong bands, the more intense at 620 nm and the other at 420 nm, respectively, with an intensity ratio of 2.30. Two similar bands are observed in the spectra of the reduced cobaloximes[15] with λ_{max} varying from 613 to 641 and from 397 to 460 nm, respectively, depending upon the nature of the axial base L, and with intensity ratios ranging from 1.09 to 1.88. Analogously, the visible spectrum of the octahedral tris(2,2′-bipyridine)cobalt(I) monocation[16] shows a band at 610 nm and a less intense band at 382 nm. Although the spectral data clearly confirm the formation of a Co(I) complex, at this stage the structure of this species is not well defined. In fact, it can be suggested that the reduction of **1** leads to the formation of a Co(I) dimer (with a Co:LE-py ratio of 1:1) which is then methylated, giving directly **2**. Alternatively, the reduction of **1** might not involve structural rearrangements. In this case, the nucleophile could consist of the $[Co^I(LE\text{-}py)_2]^-$ monoanion which, under alkylation, loses a LE-py unit, giving a mononuclear methyl derivative as a precursor of **2**. The available literature data seem to support the latter hypothesis. In fact, it has been shown that the [tris(2,2′-bipyridine)cobalt(III)]$^{3+}$ trication does not change its coordination sphere upon reduction to the corresponding Co(I) structurally characterized species.[17] Furthermore, the formation of the octahedral complex $[(n\text{-Pr})Co^I(dmgBF_2)_2py]^{2-}$, where $dmgBF_2$ = (difluoroboryl)dimethylglyoximato, is suggested to be achieved by controlled-potential electrolysis of the analogous neutral Co(III) complex.[18]

The synthesis, characterization, and solution studies of these and other similar complexes with various alkyl groups as well as the investigation of the mechanism of the formation reaction are in progress.

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Supporting Information Available: Listings of crystallographic data and refinement details, anisotropic thermal parameters for non-hydrogen atoms, positional parameters for all atoms, and complete bond lengths and angles (10 pages). Ordering information is given on any current masthead page.

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(13) (a) Simonov, Yu. A.; Zavodnik, V. E.; Shkurpelo, A. I.; Bologa, O. A. *Zh. Strukt. Khim.* **1985**, *26*, 99. (b) Simonov, Yu. A.; Malinovskii, S. T.; Bologa, O. A.; Zavodnik, V. E.; Adrianov, V. I.; Shibanova, T. A. *Kristallografiya* **1983**, *28*, 682. (c) Ablov, A. V.; Simonov, Yu. A.; Malinovskii, S. T.; Bologa, O. A.; Malinovskii, T. I. *Dokl. Akad. Nauk SSSR* **1975**, *221*, 605.

(14) McFadden, D. L.; McPhail, A. T. *J. Chem. Soc., Dalton Trans.* **1974**, 363.

(15) Schrauzer, G. N.; Windgassen, R. J.; Kohnle, J. *Chem. Ber.* **1965**, *98*, 3324.

(16) Kaizu, Y.; Torii, Y.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3296.

(17) Szalda, D. J.; Creutz, C.; Mahajan, D.; Sutin, N. *Inorg.Chem.* **1983**, *22*, 2372.

(18) Shi, S.; Daniels, L. M.; Espenson, J. H. *Inorg. Chem.* **1991**, *30*, 3407.