Coordination Compounds

Tuning a Metal's Oxidation State: The Potential of Clathrochelate Systems**

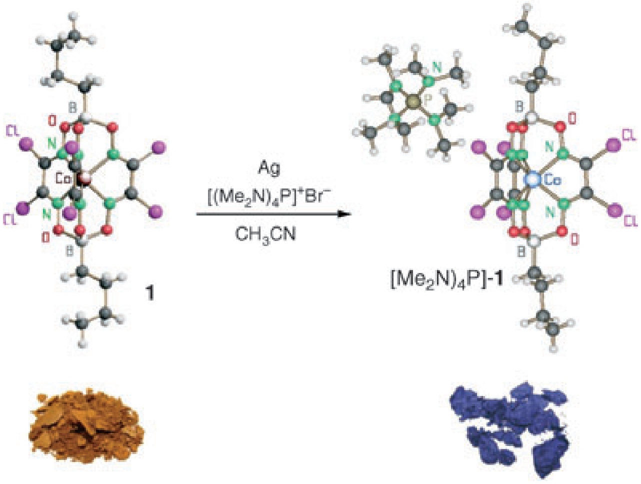
Yan Z. Voloshin, Oleg A. Varzatskii, Ivan I. Vorontsov, and Mikhail Yu. Antipin*

"Oxidation state" is one of most fundamental concepts in chemistry. The stabilization of previously unknown or unusual oxidation states of metal ions allows us to obtain results that are important both for theoretical inorganic chemistry and for the design of new molecular electronic devices, electrochromic materials, and electron-storage systems.

Complexes with a metal ion encapsulated in a three-dimensional macropolycyclic ligand cavity have undoubted promise in stabilizing unusual oxidation states of such caged ions. This is due to the fact that an encapsulated and coordinatively saturated metal ion is completely isolated from environmental factors (in particular, effects of solvation and additional coordination that exclude occurrence of redox processes by bridge mechanisms). The size of a three-dimensional ligand cavity may be controlled by changing the nature of the capping and chelating fragments of the macropolycyclic framework, and donor atoms (groups) that are optimal for stabilization of a desired electronic configuration of this ion may be chosen.[1]

Varying the substituents on a clathrochelate framework is thought to be a new and unique opportunity to stabilize unusual oxidation states of an encapsulated metal ion: although the apical substituents in the capping fragments of the same type affect the electronic characteristics of ligand donor atoms (and, therefore, the encapsulated metal ion) to a very minor extent,[2] the influence of electron-donating (electron-withdrawing) substituents in chelate (ribbed) fragments with a system of conjugated π-bonds may prove to be crucial.[3] We suppose that the electron-withdrawing substituents in such fragments of a clathrochelate ligand stabilize the lowest oxidation states of an encapsulated metal ion. A new approach to the synthesis of cobalt(I) complexes uses a macrobicyclic hexachloride ligand with six strongly electron-withdrawing substituents in chelating π-conjugated α-dioximate fragments. The template condensation of dichloroglyoxime with the corresponding boron-containing Lewis acid on a Co^{2+} ion matrix leads to formation of the brown *n*-butylborane-capped hexachloride cobalt(II) clathrochelate $[Co\{(Cl_2Gm)_3(B\textit{n}\text{-}C_4H_9)_2\}]$ (**1**) in high yield (Gm = glyoxime).

We were unable to oxidize, either chemically or electrochemically, the clathrochelate **1** to the corresponding cobalt(III) complex (the process is irreversible and is accompanied by destruction of the clathrochelate structure), but **1** easily undergoes a chemical reduction in acetonitrile solution with silver in the presence of tetraalkylammonium or tetra(dimethylamido)phosphonium halides to produce the dark-blue complex $\mathbf{1}^-$ in high yield (Scheme 1). Analogous reductions were also carried out for phenylboronic and fluoroboronic hexachloride cobalt(II) clathrochelates. The resulting tetraalkylammonium and tetra(dimethylamido)phosphonium salts of clathrochelate anions with an encapsulated Co^+ ion proved to be air-stable as solid for several months.



Scheme 1. Reduction of cobalt(II) clathrochelate **1** affords cobalt(I) clathrochelate $[(NMe_2)_4P]$-**1**.

The X-ray crystallography data for **1** and $[(NMe_2)_4P]$-**1** indicate that the Co–N distance changes very little on passing from a cobalt(II) clathrochelate **1** to a cobalt(I) clathrochelate anion $\mathbf{1}^-$ (1.984(1) vs. 2.003(3) Å, respectively), as is the case for the previously studied pair $[Co^{II}(bipy)_3]^{2+}/[Co^{I}(bipy)_3]^+$ (2.128 vs. 2.11(2) Å[4]; bipy = 2,2′-bipyridyl) due to an appreciable contribution of Co^I-to-cage charge transfer (πd→π*cage back donation). However, the Co–N distance in the synthesized clathrochelate complexes with a rigid cage framework, as in the case of macrobicyclic iron(II) compounds,[1] is substantially shorter than that in their nonmacrocyclic analogs.[4]

The coordination polyhedra of nonmacrocyclic tris-diiminate complexes and their clathrochelate analogs are also appreciably different: cobalt(II) and cobalt(I) tris-bipyridinates display a trigonal-antiprismatic (TAP) configuration

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[*] Prof. Y. Z. Voloshin
Nesmeyanov Institute of Organoelement Compounds
119991 Moscow (Russia)
Fax: (+7) 095-135-5085
E-mail: voloshin@ineos.ac.ru
voloshin@cc.nifhi.ac.ru
and
Karpov Institute of Physical Chemistry
10 Vorontsovo Pole, 105064 Moscow (Russia)
Fax: (+7) 095-975-2450
Dr. O. A. Varzatskii
Vernadskii Institute of General and Inorganic Chemistry
Kiev-142 03680 (Ukraine)
Dr. I. I. Vorontsov, Prof. M. Yu. Antipin
Nesmeyanov Institute of Organoelement Compounds
119991 Moscow (Russia)

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with distortion angles φ (in passing from TAP ($\varphi = 60°$) to a trigonal prism (TP; $\varphi = 0°$)) of 44.9° and 45.2°, respectively, whereas the geometry of the cage complexes obtained is close to the value for a TP (φ value of 7.8° and 1.3° for cobalt(II) and cobalt(I) cages, respectively). Such a geometry in the case of macrobicyclic systems is due to the large ionic (Shannon) radius of the Co^{2+} ion, which fits the cavity size of the TAP clathrochelate ligand poorly. A change in the ligand geometry from TAP, characteristic of cobalt(III) clathrochelates,[1] to TP leads to an increase in the cavity size, and this facilitates encapsulation of the Co^{2+} ion. A further rotary–translationary extension of the clathrochelate framework permits the encapsulation of a Co^{+} ion with a higher Shannon radius.

It should also be emphasized that the Co^{2+} ion is shifted (by 0.3 Å) from the cavity center towards one of the three chelating fragments (probably due to the structural Jahn–Teller effect for a low-spin d^7 configuration: according to the magnetic susceptibility data for **1**, $\mu_{eff} = 1.55\,\mu_B$ and $S = 1/2$). On the other hand, the clathrochelate of the Co^{+} ion (d^8 configuration) is a high-spin complex ($\mu_{eff} = 2.85\,\mu_B$ and $S = 1$). The X-band EPR spectrum of **1** recorded at 10 K for a powdered sample of an isostructural diamagnetic iron(II) clathrochelate containing the same ligand that was doped with 1 % of **1** shows the strong anisotropy of the *g*-factor as well as the hyperfine coupling constant. This spectrum can be described in terms of an $S = 1/2$ spin doublet interacting with a single ^{59}Co nucleus ($I = 7/2$, natural abundance 100 %) and is typical of low-spin d^7 systems.[5] The EPR spectral parameters are $g_x = 2.252$, $g_y = 2.070$, and $g_z = 1.984$ and $A_{xx} = 125 \times 10^{-4}$, $A_{yy} = 9 \times 10^{-4}$, and $A_{zz} = 50 \times 10^{-4}\,cm^{-1}$. We failed to observe the EPR spectra of paramagnetic complexes $\mathbf{1}^-$ down to 4 K because of both the long spin–lattice relaxation time and the magnitude and sign of the spin–orbital interaction and their ligand-field symmetry.[6] On the other hand, the absence of EPR signals undoubtedly excludes the formation of organic radicals (i.e., the reduced cage).

XPS was used to directly probe the cobalt ion oxidation states in **1** and $\mathbf{1}^-$. For this ion there is a noticeable (0.9 eV) decrease in the $Co\,2p_{3/2}$ binding energy in $\mathbf{1}^-$ (main peak at 780.8 eV) compared to **1** (main peak at 781.7 eV).

The UV/vis spectra of these clathrochelates in solution are different (Figure 1): the spectrum of the dark-blue solution of $\mathbf{1}^-$ contains two intense bands at $\lambda = 544$ ($\varepsilon = 6.6 \times 10^3\,mol^{-1}\,L\,cm^{-1}$) and 680 nm ($\varepsilon = 8.0 \times 10^3$), whereas the brown color of **1** is determined by two less-intense bands at $\lambda = 421$ ($\varepsilon = 640$) and 468 nm ($\varepsilon = 1550$). The intense bands in the visible spectra of cobalt(I) complexes with azomethine ligands were assigned in earlier studies[7] to charge-transfer bands (first of all to MLCT bands).

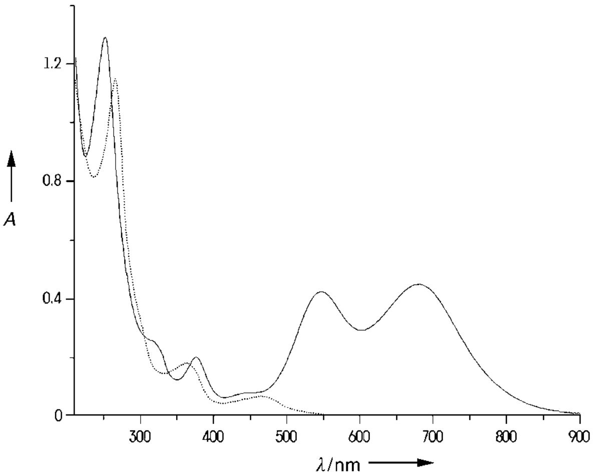

Figure 1. UV/vis spectra of acetonitrile solutions of **1** (•••••) and $[(NMe_2)_4P]$-**1** (——) at the same concentrations.

The electrochemical behavior of $\mathbf{1}^-$ in dichloromethane solution is characterized by two consecutive oxidations. The first wave, at $E_{1/2} = -440$ mV, is reversible on both glassy carbon and Pt electrodes: the Tomeš criterion value, which was determined from the cyclic voltammogram on a Pt ultramicroelectrode, is equal to 60 mV, and the ratio of peak currents for direct (anodic) and reverse (cathodic) waves on a glassy carbon electrode is close to 1. This process is assigned to a metal-based $Co^{+/2+}$ redox couple. The second wave, which is observed at higher potential ($E_{1/2} = 630$ mV), is most probably irreversible since the Tomeš criterion value is 130 mV and the above-mentioned ratio is less than 1. This process is assigned to the $Co^{2+/3+}$ redox couple.

The cobalt(II) clathrochelate can be both irreversibly oxidized and reversibly reduced electrochemically. The location and shape of the reduction wave for this complex coincide with the first oxidation wave for the cobalt(I) compound. The oxidation wave for **1** coincides with the second oxidation wave for $\mathbf{1}^-$.

Our results suggest wider possibilities for the stabilization of the lowest and highest (including unusual and previously unknown) oxidation states by introducing electron-withdrawing (in particular, halide, alkoxy and aryloxy) and electron-donating (especially amine) substituents in the chelating fragments of a macrobicyclic ligand.

Experimental Section

Single crystals of complexes **1** and $[(NMe_2)_4P]$-**1** were grown at room temperature from benzene/isooctane and dichloromethane/benzene mixtures, respectively.

Crystallographic measurements were performed at 110 K (**1**) and 120 K ($[(NMe_2)_4P]$-**1**) with a Bruker SMART 1 K CCD area detector using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å).[8] Reflection intensities were integrated with SAINT software[8] and corrected by a semi-empirical method (SADABS program).[9] The structures were solved by direct methods and refined by full-matrix least-squares in the anisotropic approximation for non-hydrogen atoms using SHELXTL.[10] The position of the hydrogen atoms was calculated geometrically and refined using the riding model with isotropic temperature factors $U_{iso} = n\,U_{eq}(C)$, where $n = 1.5$ for methyl groups and 1.2 for the other ones and U_{eq} is the equivalent isotropic displacement parameter of the corresponding pivot carbon atoms.

Crystal data for **1**: $C_{14}H_{18}B_2Cl_6CoN_6O_6$, $M_r = 659.59$, monoclinic, space group $C2/c$, $a = 17.347(4)$, $b = 8.102(2)$, $c = 17.172(3)$ Å, $\beta = 91.936(4)°$, $V = 2411.9(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.816\,g\,cm^{-3}$, $2\theta_{max} = 50.0°$, 11685 unique data, $R_1 = 0.0466$, $R_w = 0.1311$.Crystal data for $[(NMe_2)_4P]$-**1**: $C_{28}H_{48}B_2Cl_6CoN_{10}O_6P$, $M_r = 944.98$, monoclinic, space group $P2_1/c$, $a = 15.405(2)$, $b = 12.381(2)$, $c = 22.627(3)$ Å, $\beta = 102.162(3)°$, $V = 4218.6(9)$ Å^3, $\rho_{calcd} = 1.488\,g\,cm^{-3}$, $2\theta_{max} = 54.1°$, 9152 unique data, $R_1 = 0.0539$, $R_w = 0.1364$. CCDC-213266 (**1**) and -213265 ($[(NMe_2)_4P]$-**1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] Y. Z. Voloshin, N. A. Kostromina, R. Krämer, *Clathrochelates: Synthesis, Structure and Properties*, Elsevier, Amsterdam, **2002**.

[2] A. M. Sargeson, *Coord. Chem. Rev.* **1996**, *151*, 89–114; Y. Z. Voloshin, O. A. Varzatskii, A. I. Stash, V. K. Belsky, Y. N. Bubnov, I. I. Vorontsov, K. A. Potekhin, M. Y. Antipin, E. V. Polshin, *Polyhedron* **2001**, *20*, 2721–2733; Y. Z. Voloshin, O. A. Varzatskii, I. I. Vorontsov, M. Y. Antipin, A. Y. Lebedev, A. S. Belov, A. V. Palchik, *Russ. Chem. Bull.* **2003**, *52*, 1552–1561.

[3] Y. Z. Voloshin, O. A. Varzatskii, A. V. Palchik, A. I. Stash, V. K. Belsky, *New J. Chem.* **1999**, *23*, 355–357; Y. Z. Voloshin, O. A. Varzatskii, T. E. Kron, V. K. Belsky, V. E. Zavodnik, A. V. Palchik, *Inorg. Chem.* **2000**, *39*, 1907–1918; Y. Z. Voloshin, V. E. Zavodnik, O. A. Varzatskii, V. K. Belsky, A. V. Palchik, N. G. Strizhakova, I. I. Vorontsov, M. Y. Antipin, *J. Chem. Soc. Dalton Trans.* **2002**, 1193–1202; Y. Z. Voloshin, O. A. Varzatskii, T. E. Kron, V. K. Belsky, V. E. Zavodnik, N. G. Strizhakova, V. A. Nadtochenko, V. A. Smirnov, *J. Chem. Soc. Dalton Trans.* **2002**, 1203–1211; Y. Z. Voloshin, O. A. Varzatskii, A. V. Palchik, N. G. Strizhakova, I. I. Vorontsov, M. Y. Antipin, D. I. Kochubey, B. N. Novgorodov, *New J. Chem.* **2003**, *27*, 1148–1155.

[4] D. J. Szalda, C. Creutz, D. Mahajan, N. Sutin, *Inorg. Chem.* **1983**, *22*, 2372–2379; M.-C. Liaw, M.-C. Cheng, S.-M. Peng, *Bull. Inst. Chem. Acad. Sin.* **1991**, *38*, 55–61.

[5] A. Rockenbauer, E. B. Zahonyi, L. I. Simandi, *J. Chem. Soc. Dalton Trans.* **1975**, 1729; A. Rockenbauer, E. B. Zahonyi, L. I. Simandi, *J. Coord. Chem.* **1972**, *2*, 53; K. A. Lance, K. A. Goldsby, D. H. Busch, *Inorg. Chem.* **1990**, *29*, 4537–4544; K. Wang, R. B. Jordan, *Inorg. Chem.* **2000**, *39*, 1823–1827.

[6] W. Low, *Paramagnetic Resonance in Solids*, Academic Press, New York, **1960**; J. W. Orton, *Electron Paramagnetic Resonance*, Iliffe Books, London, **1968**; *Electron Paramagnetic Resonance* (Ed.: S. Geschwind), Plenum, New York, **1972**; R. L. Carlin, *Magnetochemistry*, Springer, Berlin, **1986**.

[7] Y. Kaizu, T. Yazaki, Y. Torii, H. Kobayashi, *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2068–2071; Y. Kaizu, Y. Torii, H. Kobayashi, *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3296–3297; A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, **1984**.

[8] *SMART and SAINT, Release 5.0, Area detector control and integration software*, Bruker AXS, Analytical X-ray Instruments, Madison, Wisconsin, USA, **1998**.

[9] G. M. Sheldrick, *SADABS: A program for exploiting the redundancy of area-detector X-ray data*, University of Göttingen, Germany, **1999**.

[10] G. M. Sheldrick, *SHELXTL-97. Program for the Solution and Refinement of Crystal Structures*, Bruker AXS Inc., Madison, Wisconsin, USA, **1997**.