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Extending the Coordination Chemistry of 1,3,5-Triaza-7-phosphaadamantane (PTA) to Cobalt Centers: First Examples of Co-PTA Complexes and of a Metal Complex with the PTA Oxide Ligand

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Water-soluble Co^{III} and Co^{II} complexes with P- or N-coordinated PTA or PTA oxide ligands, respectively, have been prepared and fully characterized, constituting the first examples of cobalt compounds bearing PTA or any ligand with a cage-like PTA core, the latter complex providing also the first PTA oxide coordination to a metal center.

The synthesis and investigation of metal complexes with 1,3,5-triaza-7-phosphaadamantane (PTA) and derived aminophosphine ligands are currently deserving an increased attention in coordination chemistry,[1] mainly because of their water solubility and interesting applications in various areas.[1–4] Group 8–10 transition metals provide the major and most studied class of PTA complexes,[1,3] including a broad spectrum of Ru, Pt, Pd, Rh and Ni compounds and, to a lesser extent, of Fe, Ir, and Os complexes.[4] However, among all of the group 8–10 transition metals, only Co has not yet been reported to form compounds with PTA. The filling of this gap constitutes an objective of the current study. Moreover, various Co coordination compounds, for instance with phosphine ligands, are of significance in catalysis, biomimetic and medicinal chemistry, molecular magnetism, and materials chemistry.[5] This constitutes a further encouragement for the preparation of the first PTA containing Co complexes.

Besides, although nearly 200 transition-metal complexes with PTA or its derivatives have already been reported, the coordination chemistry of its oxide (PTA═O) has remained unexplored with the exception of one recent boron adduct $[BH_3(PTA{=}O)]$.[4j] As a ligand, PTA═O should not exhibit the usual P-coordination mode known for PTA itself (coordination through a N atom is still rarely observed),[4j,l,6] and thus a second aim of our work consists of the preparation of a PTA═O metal complex bearing the unusual N-coordination mode of the PTA core.

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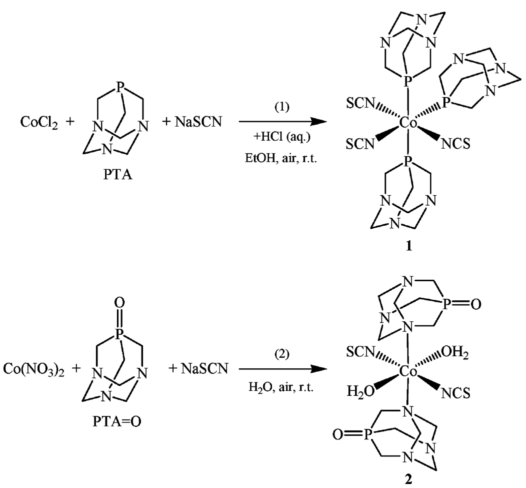
Recently, we have extended[7] the rapidly growing family of transition-metal PTA complexes to Cu and found an easy route for the synthesis of Cu^IPTA compounds based on a redox reaction of a Cu^{II} salt with PTA at ambient temperature. By employing a related synthetic approach to Co^{II} centers, we have now succeeded in the preparation of the Co^{III} P-coordinated PTA compound *mer*-$[Co(NCS)_3(PTA)_3]\cdot EtOH$ (**1**) and of the Co^{II} N-coordinated PTA=O complex *trans*-$[Co(NCS)_2(PTA{=}O)_2(H_2O)_2]$ (**2**) (complex with the OC-6–13 IUPAC configuration index), which, to our knowledge, constitute the first cobalt complexes bearing PTA or any other ligand with a PTA core. Besides, compound **2** represents the first example of PTA oxide coordination to a metal center.

The combination in an ethanolic medium, at room temperature and in air, of anhydrous $CoCl_2$ with PTA, followed by the addition of an acidic (HCl) ethanolic solution of sodium thiocyanate (Scheme 1, reaction 1), provides the formation of a neutral Co^{III}PTA compound with NCS^- as the auxiliary ligand, **1**, which has been isolated as a brownish-red air-stable solid in ca. 55% yield (based on $CoCl_2$). Attempts to obtain any CoPTA compound in the absence of NCS^- have failed. The formation of **1** involves an unexpected redox process resulting in the oxidation, by dioxygen of air (no evident reaction is observed under an inert atmosphere) and in an acidic medium, of Co^{II} to Co^{III}, overcoming the common ability of PTA to act as a reductant of group 8–10 metal centers (e.g., Pt, Pd, Ni, and Ru),[8] thus tending to stabilize lower metal oxidation states. The use of anhydrous $CoCl_2$ as the metal source and ethanol as the solvent is essential for the synthesis of **1** because replacements of that metal salt by hydrated cobalt(II) chloride or nitrate or of ethanol by water or methanol do not afford **1** or any related compound. This conceivably can be accounted for, at least when using hydrated $CoCl_2$ or water as the solvent, by the formation of aquacobalt(II) species, inert to H_2O ligand exchange (e.g., with P-donor species) and stable toward oxidation. In contrast, if PTA=O is employed instead of PTA, an aqueous medium can be used and, upon reaction with aqueous $Co(NO_3)_2$, the aquacobalt(II) complex **2** with N-coordinated PTA=O is obtained (Scheme 1, reaction 2), being isolated as pink-orange crystals. Both compounds **1** and **2** are water-soluble and have been characterized by IR spectroscopy and elemental and single-crystal X-ray diffraction structural analyses.[9] Complex **1** has also been analyzed by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy, while **2** is paramagnetic.

The IR spectra of **1** and **2** exhibit a set of vibrations in the 1475−460 cm^{-1} range, typical of the coordinated PTA core, as well as a very intense ν(CN) band at 2079 or 2085 cm^{-1} for **1** or **2**, respectively, and medium or weak ν(CS) absorptions in the 840–780 cm^{-1} range, in accordance with the terminal N-bonded thiocyanate ligands.[10] Compound **2** also possesses a strong ν(P=O) band with a maximum at 1165 cm^{-1}, typical for PTA oxide.[1] The ^1H and $^{13}C\{^1H\}$ NMR spectra of **1** reveal the expected resonances at typical chemical shifts for PTA ligands[1,4,7] (and ethanol of crystallization). Its $^{31}P\{^1H\}$ NMR spectrum in DMSO-d_6 [triplet and doublet at δ 8.9 and −10.9, respectively, with $^2J(PP) = 38$ Hz] is indicative of the meridional configuration of the phosphines, as in the solid state (Figure 1).

Scheme 1. Synthesis of **1** and **2**



The molecular structure of **1** (Figure 1) exhibits a rather distorted octahedral environment about the Co center filled by three neutral PTA and three thiocyanate ligands in the meridional configuration, adopting the most common monodentate P- or N-coordination modes,[1,11] respectively. The major deviation from the octahedral geometry concerns the P3−Co−P1 angle [164.66(8)°] of the two *trans*-PTA ligands bound to Co through the corresponding Co−P3 [2.218(3) Å] and Co−P1 [2.269(3) Å] bonds. These bond lengths concerning the mutually *trans*-PTA ligands are slightly elongated relative to the Co−P2 distance [2.182(2) Å], presumably because of a stronger trans influence of PTA than NCS^-. In accordance, the Co−N2 bond of 1.947(6) Å (involving the NCS^- ligand trans to PTA) is ca. 0.06 Å

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(9) Crystal data for **1**: $C_{23}H_{42}CoN_{12}OP_3S_3$, MW = 750.74, red needles, 0.22 × 0.06 × 0.01 mm, Cu Kα radiation, $\lambda = 1.541\,80$ Å, monoclinic, space group *P*21, $a = 9.703(7)$ Å, $b = 15.243(12)$ Å, $c = 10.459(8)$ Å, $\beta = 92.80(6)°$, $V = 1545(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.614$ g cm $^{-3}$, μ(Cu Kα) = 8.08 mm^{-1}, $T = 100(2)$ K, no. of collected reflns = 11 947, no. of unique reflns = 5434, no. of reflections with $I > 2\sigma(I)$ = 3016 ($R_{int} = 0.0951$), Flack parameter = −0.013 (5), R1 = 0.0509, wR2 = 0.0630. Crystal data for **2**: $C_{14}H_{28}CoN_8O_4P_2S_2$, MW = 278.72, pink-orange needles, 0.38 × 0.08 × 0.08 mm, Mo Kα radiation, λ = 0.710 73 Å, monoclinic, space group *P*21/*c*, $a = 7.781(3)$ Å, $b = 14.375(6)$ Å, $c = 10.002(4)$ Å, $\beta = 91.74(4)°$, $V = 1118.2(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.656$ g cm^{-3}, μ(Mo Kα) = 1.14 mm^{-1}, $T = 100(2)$ K, no. of collected reflns = 7481, no. of unique reflections = 2595, no. of reflections with $I > 2\sigma(I)$ = 2078 ($R_{int} = 0.043$), R1 = 0.0498, wR2 = 0.1242.

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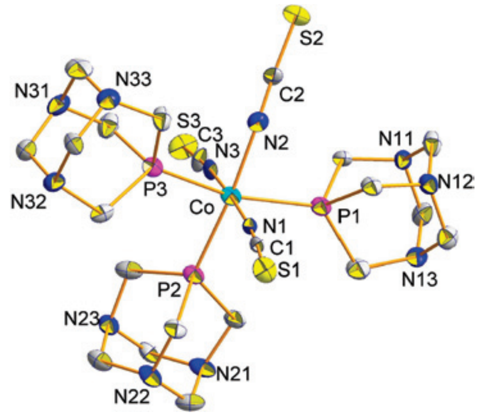

Figure 1. Thermal ellipsoid plot of **1** with a partial atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Crystallization ethanol molecule and H atoms are omitted for clarity. Selected bond distances (Å): Co−N1 1.882(6), Co−N2 1.947(6), Co−N3 1.890(6), Co−P1 2.269(3), Co−P2 2.182(2), Co−P3 2.218(3).

lengthened in comparison with the Co−N1 [1.882(6) Å] and Co−N3 [1.890(6) Å] bonds for the mutually *trans*-thiocyanates (Figure 1).

The binding Co−N2−C2 angle [161.7(5)°] of the thiocyanate ligand that is trans to the P2 atom is lower than the corresponding Co−N1−C1 and Co−N3−C3 angles of 174.9(6) and 171.7(6)°, respectively. No disorder is observed among the thiocyanate ligands, which adopt almost a linear geometry with the N−C−S angles ranging from 175.7(7) to 178.0(7)° [av 177.2(7)°], being within the typical values for Co(NCS) species.[11] The average Co−P and Co−N distances of ca. 2.22 and 1.90 Å, respectively, are comparable to those previously reported for other cobalt complexes bearing phosphine and thiocyanate ligands.[12] All PTA ligands exhibit nearly equivalent geometrical arrangements if viewed along the P−Co bond and contain similar cagelike PTA cores (Figure 1). The bonding parameters of such cores are commonly affected by protonation of one N atom,[7,8c,13,14] which does not occur in compound **1**, in spite of its crystallization from an acidic solution.

The crystal structure of **2** (Figure 2) is composed of discrete monomeric units, with a Co^{II} atom lying on an inversion center and possessing a slightly distorted octahedral coordination geometry. It can be viewed as bearing two N-bound PTA═O ligands in axial positions, as well as two N-coordinated thiocyanate moieties and a pair of water ligands in equatorial sites. All of them are symmetrically equivalent and mutually trans-oriented. The Co−N1 [2.358(3) Å] and Co−N10 [2.068(3) Å] bonds are significantly elongated relative to the corresponding Co−P [av 2.22(2) Å] and Co−N$_{NCS}$ [av 1.90(2) Å] in **1** but comparable to those of related compounds with hexamethylenetetramine.[15] The P−O1 distance of 1.496(3) Å is similar to the corresponding ones in free PTA oxide (ca. 1.476 Å) and in the boron PTA═O adduct [1.490(1) Å].[4j] An interesting feature consists in the presence of extensive intermolecular hydrogen-bonding interactions. Hence, each water molecule O2 acts as a double-hydrogen-bond donor to the PTA═O O atom [O2−H21···O1^{i} 2.659(4) Å] and to one of the N atoms of the PTA core [O2−H22···N2^{ii} 2.830(4) Å], thus strongly and multiply linking neighboring mononuclear units into a three-dimensional hydrogen-bonded supramolecular assembly (for further details, see Figure S1 in the Supporting Information).

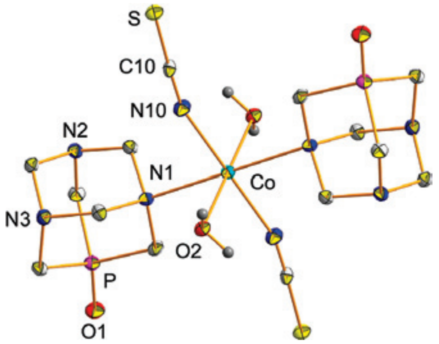

Figure 2. Thermal ellipsoid plot of **2** with a partial atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Methylene H atoms are omitted for clarity. Selected bond distances (Å): Co−O2 2.062(3), Co−N1 2.358(3), Co−N10 2.068(3), P−O1 1.496(3).

In summary, we have reported the first Co compounds bearing PTA or any aminophosphine ligand with a PTA core, thus completing the broad and extensively growing family of the group 8–10 transition-metal PTA complexes with Co examples. Besides, compound **2** also provides the first case of PTA oxide coordination to a metal center and expands the still rarely observed N-coordination ability of the PTA core.[4j,l,6] The reaction parameters, such as the type of starting cobalt salt, auxiliary ligand, and solvent and its pH, are important for the described syntheses and thus should be thoroughly accounted for on attempting the preparation of further CoPTA complexes. The extension of these studies toward widening of the series of water-soluble CoPTA and transition metal PTA═O compounds, e.g., to various auxiliary ligands and N-alkylated PTA cores, is currently underway.

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Supporting Information Available: Synthetic procedures for **1** and **2**, full experimental details, crystal packing diagram of **2** (Figure S1), NMR, IR, and UV spectra, and crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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