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Radial Trinuclear Complexes of Cobalt(II) and Nickel(II) with Tris(2-dimethylphosphinoethyl)-amine

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The tri(tertiary phosphine) ligand tris(2-diphenylphosphinoethyl)amine, $N(CH_2CH_2P(C_6H_5)_2)_3$ or np_3, has shown a number of interesting characteristics. Due to its flexibility it can form transition metal complexes with coordination numbers ranging from four to six and geometries approaching the idealized forms of the trigonal pyramid [1], trigonal bipyramid [2], square pyramid [3] or octahedron [4]. Moreover, when the nitrogen atom is not coordinated, a tetrahedral geometry of the complex is observed [5].

We have now synthesized a new ligand having the inner skeleton of np_3, but having methyl substituents in place of the terminal phenyl groups, *i.e.* tris(2-dimethylphosphinoethyl)amine, $N(CH_2CH_2P(CH_3)_2)_3$ or $Menp_3$. The ligand differs from np_3 both in its donor capacity and steric properties. The ligand $Menp_3$ reacts with cobalt(II) and nickel(II) salts invariably giving trinuclear complexes where metal centers are coordinated only to phosphorus and nitrogen atoms, even when other strong coordinating agents are present in the reaction mixture. The compounds, isolated thus far, have formulae $[M_3(Menp_3)_4](BF_4)_6 \cdot 4DMF$ (M = Co, Ni) and $[Ni_3(Menp_3)_4]Br_3(BPh_4)_3$. The nickel complexes are air stable, while the cobalt complex decomposes rapidly in solution and more slowly in the solid state. All the complexes are moderately soluble in polar solvents such as nitroethane, acetonitrile or DMF. The nickel complexes are diamagnetic. The cobalt complex has a magnetic moment of 1.96 μ_B, which is practically constant from room to liquid nitrogen temperature.

A X-ray analysis of the complex $[Co_3(Menp_3)_4(BF_4)_6] \cdot 4DMF$ has been carried out. A perspective view of the complex cation is shown in Figure. The structure consists of three five-coordinated metal atoms with distorted trigonal bipyramidal geometry. One apical and the three equatorial positions of each trigonal bipyramid are occupied by the nitrogen and the three phosphorus atoms of one $Menp_3$ ligand. The other apical site, as well as those of the two other trigonal bipyramidal moieties, is occupied by a phosphine group of a fourth $Menp_3$ ligand which bridges the three trigonal bipyramidal units. The whole complex has C_{3v} symmetry. In order to hold together the three metal atoms, the central $Menp_3$ ligand is almost completely flattened, the nitrogen atom being less than 0.1 Å out of the plane of the three phosphorus atoms. Bond distances and angles within the complex cation (see Figure) compare well with those found in other low spin cobalt(II) complexes having a distorted TBP geometry [6].

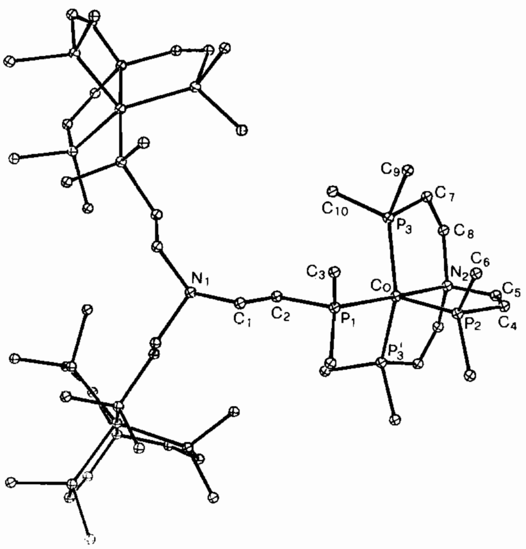

Figure. Perspective drawing of the complex cation. All atoms are assigned a unique temperature factor. Independent bond distances (Å) and angles (deg) of interest are: Co–P(1) = 2.25(2), Co–P(2) = 2.26(1), Co–P(3) = 2.26(1), Co–N(2) = 2.05(5), P(1)–Co–P(2) = 96.5(6), P(1)–Co–P(3) = 94.0 (5), P(2)–Co–P(3) = 106.4(5), P(3)–Co–P(3)′ = 145.1(6), N(2)–Co–P(1) = 177.3(1.2), N(2)–Co–P(2) = 86.1(1.2), N(2)–Co–P(3) = 85.2(8).

Reflectance and absorption spectra of each complex in acetonitrile are substantially similar. In particular the electronic spectrum of the cobalt derivative, with bands at 9,300 and 18,200 cm^{-1} and shoulders at 25,000 and 31,500 cm^{-1}, is of the type found for other low-spin cobalt(II) complexes with distorted TBP geometry [6]. The spectra of the two nickel complexes are almost identical, with a strong band at 20,000 cm^{-1} and a week shoulder at 26,500 cm^{-1}. On the basis of their spectra, the nickel complexes are assigned a TBP geometry [7]. Thus, the structure of these complexes is probably the same as that found by X-ray diffraction for the cobalt derivative.

Of particular interest are the conductivity data, since this type of hexa-charged cation is still quite rare in the literature. Solutions of approximately 10^{-3} *M* of the tetrafluoroborates of the cobalt and nickel complexes in acetonitrile have values of molar conductivity of 643 and 576 ohm^{-1} cm^2 mol^{-1}, respectively. A conspicuous decrease of the value to 370 ohm^{-1} cm^2 mol^{-1} for 10^{-3} *M* solution of the complex $[Ni_3(Menp_3)_4]Br_3(BPh_4)_3$ in the same solvent is to be ascribed either to reduced mobility of the tetraphenylborate anions or to the formation of ionic pairs [8]. On the other hand, the possible coordination of the halide ions to the cobalt atoms is excluded on the basis of the UV spectra. These conductivity data are comparable with the few data available for 1:6 electrolytes [9].

Experimental

All operations were carried out under a nitrogen atmosphere.

The tris(2-dimethylphosphinoethyl)amine ligand, $Menp_3$, was synthesized by the following reaction:

$$3(CH_3)_2PNA + N(CH_2CH_2Cl)_3 \xrightarrow[-78\ ^\circ C]{\text{liq. } NH_3} N(CH_2CH_2P(CH_3)_2)_3 + 3NaCl$$

$(CH_3)_2PNa$ and $N(CH_2CH_2Cl)_3$ were prepared according to literature methods [10, 11]. After the ammonia had been evaporated the phosphine was extracted with diethyl ether and vacuum distilled at 140 °C/0.6 torr. The yield was *ca.* 60%. This compound is a colorless liquid, sensitive to air. *Anal.* Calcd for $C_{12}H_{30}NP_3$: C, 51.23; H, 10.75; N, 4.98; P, 33.10. Found: C, 51.34; H, 10.76; N, 4.76; P, 32.90. The proton NMR spectrum shows a eighteen-proton doublet at 9.08 τ, a six-proton multiplet centered at 8.60 τ and a six-proton multiplet at 7.51 τ which are assigned to the $>P\text{–}CH_3$, $>P\text{–}CH_2$ and $>N\text{–}CH_2$ protons, respectively.

The complexes $[M_3(Menp_3)_4](BF_4)_6\cdot 4DMF$, M = Co, Ni, were prepared by mixing, at room temperature, solutions of the $Menp_3$ ligand and the metal salt in DMF. The crystals, dark green or red for the cobalt and nickel derivative, respectively, precipitated after *ca.* 3 hours. The complex $[Ni_3(Menp_3)_4]Br_3(BPh_4)_3$ was obtained as red crystals by reacting $NiBr_2$, $Menp_3$ and $NaBPh_4$ in butanol/DMF. *Anal.* $[Co_3(Menp_3)_4](BF_4)_6\cdot 4DMF$ [12]; calcd for $C_{60}H_{148}B_6Co_3F_{24}N_8O_4P_{12}$: C, 34.07; H, 7.05; Co, 8.35; N, 5.29; P, 17.57; found: C, 33.72; H, 7.14; Co, 7.90; N, 5.12; P, 17.35. $[Ni_3(Menp_3)_4](BF_4)_6\cdot 4DMF$ [12]; calcd for $C_{60}H_{148}B_6Ni_3F_{24}N_8O_4P_{12}$: C, 34.08; H, 7.05; Ni, 8.33; N, 5.29; P, 17.57; found: C, 32.67; H, 7.15; N, 4.85; Ni, 7.80; P, 17.85. $[Ni_3(Menp_3)_4]Br_3(BPh_4)_3$; calcd for $C_{120}H_{180}B_3Br_3N_4Ni_3P_{12}$: C, 57.68; H, 7.26; Br, 9.59; N, 2.24; Ni, 7.05; P, 14.87; found: C, 57.70; H, 7.72; Br, 9.86; N, 2.47; Ni, 7.00; P, 15.10.

The compound $[Co_3(Menp_3)_4](BF_4)_6\cdot 4DMF$ crystallizes in the hexagonal space group $P6_3mc$, with $a = 21.634(8)$ and $b = 12.650(5)$ Å. D_c for two unit formulae $C_{55}H_{148}N_8P_{12}O_4F_{24}B_6Co_3$ in the cell is 1.331 g/cm^3. 570 reflections out of 1125 measured with a Philips PW1100 automated diffractometer were labelled as observed (I $(I \geq 3\sigma(I))$. The structure was solved by direct methods using the program MULTAN. A long series of F_o and F Fourier maps was required to complete the model. Even at the end of least sqaures refinement ($R = 0.093$, $R_w = 0.112$, anisotropic temperature factors being used for Co, P, N, F atoms) disorder is observed in the several fragments of the molecule. Thus, the alphatic chains of the terminal $Menp_3$ ligands, which are symmetry constrained to lie on mirror planes, show a tendency to diverge from these planes. Whenever possible two distinct positions, half populated, were located on each side of the plane (atom C(5)); for most atoms the effect is limited to high temperarure factors and appreciable deviations of bond distances and angles from their normal values. Furthermore, the tetrafluoroborate anions are highly disordered and more than four positions were refined for the fluorine atoms of each BF_4^- group. Finally only parts of the DMF molecule could be located. Significant, however, is the fact that these molecules lie at such point symmetries that their total number in the cell is eight, in good agreement with the elemental analysis.

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