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The Crystal and Molecular Structure of a Mixed Ligand Complex: Tetramethylethylenediamine-bis-(O,O′-diethylphosphorodithioato)nickel(II)

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Five- and six co-ordinate mixed ligand complexes are formed by the addition of amines to square planar bis(O,O′-dialkylphosphorodithioato)nickel(II) chelates.[1] The molecular structures of a series of bis-(O,O′-dialkylphosphorodithioato)nickel(II) adducts with aromatic heterocyclic amines (pyridine, 2,2′-bipyridyl, 1,10-phenanthroline) have been investigated by X-ray diffraction (see ref. 1 for a review), but the adducts with aliphatic amines are seldom stable enough to be isolated in solid state. Their formation in solution is however firmly established.[1]

We wish to report a single crystal X-ray analysis of tetramethylethylenediamine-bis(O,O′-diethylphosphorodithioato)nickel(II), which is the first example of a tertiary aliphatic amine adduct of a bis(O,O′-dialkylphosphorodithioato)nickel(II) complex. The compound was prepared by reaction between N,N′-tetramethylethylenediamine (TMED) and bis(O,O′-diethylphosphorodithioato)nickel(II) and suitable green crystals were grown by slow evaporation of an acetone solution.[2]

Crystal Data

$C_{14}H_{36}N_2NiO_4P_2S_4$, M = 545.0, monoclinic, a = 22.281(2), b = 21.597(2), c = 13.237(3) Å, β = 126.42(2)°, U = 5126.1 Å^3, Z = 8, D_c = 1.48 g ml^{-1}, space group $P2_1/n$. Mo-Kα radiation.

Solution and Refinement

Data for some 6300 observed reflexions were collected on a Hilger and Watts four circle diffractometer. The positions of the two nickel atoms in the asymmetric unit were determined using the direct method program MULTAN. The other non-hydrogen atoms were then located by a series of Fourier syntheses and least squares refinements. Refinement has reached a conventional R of 0.09 and is continuing.

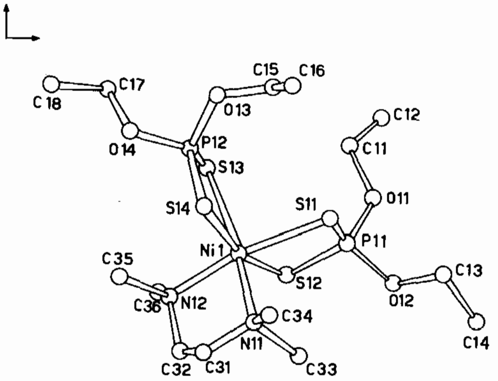

Figure 1. Projection of molecule I in the yz plane.

TABLE I. Bond Lengths (Å) in Some Bis(O,O′-diethylphosphorodithioato)nickel(II) Adducts with Amines.

Compound	Ni–S	Ni–N	P–S	P–O	Refs.
Ni(Etdtp)$_2$	2.21	–	1.97	1.63	3
Ni(Etdtp)$_2$·2py	2.49	2.11	1.98	1.58	4
Ni(Etdtp)$_2$·phen	2.49	2.10	1.97	1.61	5
Ni(Etdtp)$_2$·TMED	2.50, 2.55	2.19	1.97, 1.98	1.59	This work

The structure consists of discrete monomeric molecules in which each nickel atom is coordinated to four sulphur atoms of the dithiophosphate groups and two nitrogen atoms of the TMED. Both types of ligand are bidentate and they close three ring systems around nickel in a distorted octahedral arrangement. A projection of molecule I in the yz plane is shown in Figure 1. The dimensions of the two independent molecules are identical within the calculated standard deviations and are discussed together here.

The dithiophosphate groups are asymmetrically coordinated to nickel giving two distinct Ni–S distances. In one set, the four distances fall between 2.547(4) and 2.554(5) Å (mean, 2.549 Å) while the spread for the shorter bonds is from 2.493(3) to 2.504(4) Å (mean, 2.504 Å). In all cases, the longer bonds are those *trans* to the nitrogen atoms of ethylenediamine groups. These two distances are reflected in the magnitudes of the P–S–Ni angles which also fall into two groups, mean values 84.4 and 85.9°, with as expected the larger angle being associated with the shorter Ni–S bond. All four NiS_2P ring systems are nearly planar but in each molecule the deviations of the atoms from the best plane are much smaller for one of the rings, *e.g.* 0.001 Å (mean) for the atoms Ni(1)S(11), P(11)S(12) compared with

0.022 Å (mean) for Ni(1)S(13)P(12)S(14). The mean Ni–N distance is 2.19 Å. Important angles at the nickel atoms have the following values: S–Ni–S (in NiS_2P ring) 79.6°, N–Ni–N (in NiN_2C_2 ring) 83.7°, S–Ni–S 88.8–95.2°, and S–Ni–N 90.7–101.3°. Mean values for other angles are S–P–S 110.1°, Ni–N–CH_2 104°, Ni–N–CH_3 114°.

In addition to there being two distinct Ni–S bond types, the bonds are slightly longer than those found in analogous complexes with aromatic heterocyclic amines (see Table I). The Ni–N bonds are however significantly longer probably as a result of crowding of the nitrogen sites and the poorer donor properties of the ditertiary aliphatic amine.

Acknowledgment

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