Crystal Structures of the Reaction Products of 1,10-Phenanthroline and Bis-(*OO*′-dimethyldithiophosphato)nickel(II)

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Summary Displacement of one or both of the chelated dimethyldithiophosphato-groups occurs when 1,10-phenanthroline reacts with bis-(*OO*′-dimethyldithiophosphato)nickel(II): three crystalline reaction products have been isolated and their structures have been determined by *X*-ray methods.

THE reaction of bidentate heterocyclic ligands containing nitrogen donor atoms with planar nickel(II) chelates of dialkyldithiophosphates can be predicted to give *cis*-adducts of the type $\mathrm{Ni[S_2P(OR)_2]_2{\cdot}X}$, where R represents an alkyl group and X the bidentate ligand. Structure determinations of the adducts in which X = 2,2′-bipyridyl and 1,10-phenanthroline have confirmed this statement.[1,2] The expectation that monodentate ligands give *trans*-adducts of the type $\mathrm{Ni[S_2P(OR)_2]_2{\cdot}2Y}$ has also been verified by an *X*-ray structure determination of the adduct in which Y = pyridine.[3] These adducts formed with monodentate and bidentate ligands may be either five- or six-co-ordinate complexes of nickel(II) and are usually paramagnetic. For example, a crystal structure determination of the adduct, $\mathrm{Ni[S_2P(OMe)_2]_2{\cdot}X}$, where X = 2,9-dimethyl-1,10-phenanthroline, showed that it was a five-co-ordinate complex of nickel(II).[2] In attempts to obtain a similar five-co-ordinate adduct with 1,10-phenanthroline and $\mathrm{Ni[S_2P(OMe)_2]_2}$, we have isolated several reaction products.

Pink crystals, (I), were isolated from acetone or ethanol solutions containing 1,10-phenanthroline and $\mathrm{Ni[S_2P(OMe)_2]_2}$ in a mole ratio of at least 3:1. If the nickel chelate is present in excess a green solution is obtained from which two distinctly different crystalline compounds, bright green hexagonal shaped crystals, (II), and yellow green needles, (III), were isolated.

(I): $\mathrm{Ni(C_{12}H_8N_2)_3{\cdot}[S_2P(OCH_3)_2]_2}$: pink crystals: $a = 24{\cdot}885(9)$, $b = 11{\cdot}313(6)$, $c = 19{\cdot}771(8)$ Å, $\beta = 131°39'(1')$, $U = 4156$ Å^3, $D_c = 1{\cdot}46$, $D_m = 1{\cdot}48$ g cm^{-3}, $Z = 8$, space group Cc or $C2/c$.

(II): $\mathrm{Ni[S_2P(OCH_3)_2]_2{\cdot}C_{12}H_8N_2}$: bright green crystals: $a = 14{\cdot}914(5)$, $b = 9{\cdot}332(3)$, $c = 23{\cdot}359(7)$ Å, $\beta = 135°57'(1')$, $U = 2301$ Å^3, $D_c = 1{\cdot}59$, $D_m = 1{\cdot}56$ g cm^{-3}, $Z = 4$, space group $P2_1/c$.

(III): $\mathrm{Ni[S_2P(OCH_3)_2]_2{\cdot}C_{12}H_8N_2}$: yellow-green crystals: $a = 6{\cdot}61(1)$, $b = 18{\cdot}57(2)$, $c = 18{\cdot}86(2)$ Å, $\beta = 100°10'(30')$, $U = 2279$ Å^3, $D_c = 1{\cdot}612$, $D_m = 1{\cdot}610$ g cm^{-3}, $Z = 4$, space group $P2_1/c$.

The structures of all three compounds were determined by single crystal *X*-ray methods and were found to be six-co-ordinate complexes of nickel(II).

A complete structure determination of (III) has been reported recently.[2] It is a six-co-ordinate paramagnetic chelate of nickel(II) ($\mu = 3{\cdot}13$ B.M.) in which two of the six co-ordination positions are occupied by nitrogen donors in the 1,10-phenanthroline molecule, and the remaining four positions by the sulphur donors in the dithiophosphate ligands. The structure of (II) was solved by the usual Patterson and Fourier techniques with 3046 statistically significant reflexions that were collected, using Mo-K_α radiation, with an automated Picker Nuclear FACS I diffractometer equipped with a graphite monochromator. The structure (with the exclusion of the hydrogen atoms) was refined by a full-matrix least-squares method with anisotropic temperature factors, and the final discrepancy factor R, was 4·7%. (II) is a six-co-ordinate paramagnetic chelate of nickel(II) ($\mu = 3{\cdot}16$ B.M.) with a molecular structure identical with that of (III). Hence, (II) and (III) are two different crystal modifications in which there is a difference in the molecular packing. In the bright green crystals, (II), the planes of the phenanthroline molecules are 3·3 Å apart and they interact in pairs. In addition, there is a weak intermolecular interaction (3·20 Å) between the oxygen atom of the methoxy-group and a carbon atom of the phenanthroline ring system. In the yellow green crystals, (III), the phenanthroline molecules are 3·4 Å apart and are packed in infinite chains in the direction of the *a*-axis. The distance between the oxygen atom of a methoxy-group and a ring carbon atom in (III) is 3·29 Å.

The structure of (I) was solved by the symbolic addition method with 1466 reflexions collected, as described for (II). The positions of all the atoms, except the hydrogen atoms, were located by successive Fourier and difference Fourier syntheses and the refinement was carried out in the space group $C2/c$ by a least-squares method with anisotropic temperature factors. The discrepancy factor R, at the present stage of the refinement is 8·6%. (I) is a six-co-ordinate chelate of nickel(II) in which all six co-ordination positions are occupied by the nitrogen donors in the three 1,10-phenanthroline molecules. A projection of the molecular structure down the b-axis is shown in the Figure. All bond distances in (I) and (II) are normal and are similar to the values that have already been reported for (III).

The reaction products of 1,10-phenanthroline with bis-(OO'-dimethyldithiophosphato)nickel(II) that have been isolated are, therefore, all six-co-ordinate chelates of nickel(II). Although a five-co-ordinate chelate, similar to that obtained with 2,9-dimethyl-1,10-phenanthroline, was not isolated, such a complex may exist in solution. There is evidence for the presence of at least one other crystalline form; a few microscopic greenish brown crystals were always found with (II) and (III), but all attempts to separate them and grow larger crystals that were suitable for an X-ray structure determination resulted in the formation of (II) and (III).

These results indicate that when the bidentate ligand, 1,10-phenanthroline, reacts with the planar nickel(II) chelate, $Ni[S_2P(OMe)_2]_2$, displacement of one or both dithiophosphato-groups will occur to give six-co-ordinate adducts. It is possible that a five-co-ordinate adduct also may be present in solution. Unless it can be unequivocally shown that only one of the possible adducts is present in solution, caution should be exercised in the interpretation of the electronic, n.m.r., and i.r. spectra of solutions containing these adducts.

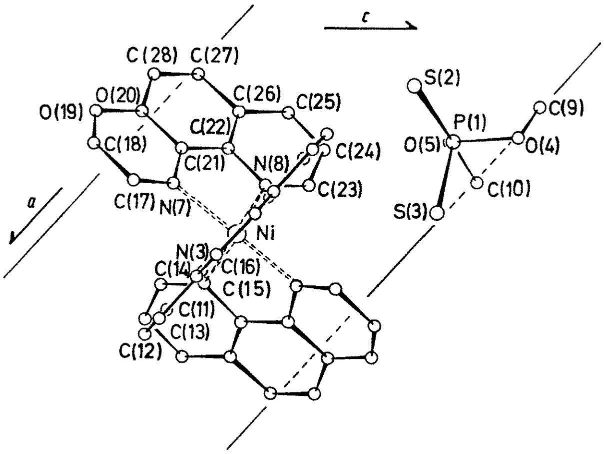

FIGURE. *Projection of a portion of the molecule,* $Ni(C_{12}H_8N_2)_3$-$[S_2P(OMe)_2]_2$ *down the* b-*axis.*

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